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REACTIONS OF ATOMIC CARBON WITH WATER

Glenn Flanagan

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REACTIONS OF ATOMIC CARBON WITH WATER

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REACTIONS OF ATOMIC CARBON WITH WATER

Glenn Flanagan

A Thesis

Submitted to

the Graduate Faculty of

Auburn University

in Partial Fulfillment of the

Requirements for the

Degree of

Master of Science

Auburn, Alabama

August 27, 1986

Thesis
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REACTIONS OF ATOMIC CARBON WITH WATER

Glenn Flanagan

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VITA

Glenn Flanagan, Lieutenant U. S. Navy, son of Samuel and Nina (Brown) Flanagan, was born August 10, 1956, in Mobile, Alabama. He attended Mobile County Parochial and Public Schools graduating from John S. Shaw High School, Mobile, in 1974. In July 1974, he entered the United States Naval Academy and was awarded the degree of Bachelor of Science (Chemistry) and commissioned an Ensign in the U. S. Navy on June 7, 1978. In September 1978, he commenced training to attain qualifications for supervision of the operation of naval nuclear propulsion plants and graduated from the Naval Nuclear Propulsion School, Orlando, Florida, in April 1979 and the Naval Nuclear Prototype Unit, Ballston Spa, New York, in September 1979. He then attended Surface Warfare Officer School, Newport, Rhode Island graduating in March 1980. He served two sea tours, from April 1980 until April 1982 in nuclear powered cruiser USS South Carolina (CGN-37) and from May 1982 until June 1984 in nuclear powered aircraft carrier USS Nimitz (CVN-68). In June 1984, he commenced graduate studies under the Navy's Post Graduate Education Program. He married Margie, daughter of Finest and Fannie (Scott) Kirksey, in September 1978. They have one son Glenn, Jr. .

THESIS ABSTRACT

REACTIONS OF ATOMIC CARBON WITH WATER

Glenn Flanagan

Master of Science, August 27, 1986
(B.S., U. S. Naval Academy, 1978)

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Atomic carbon reacts with water to produce formaldehyde via a carbene intermediate, hydroxymethylene. Hydroxymethylene further reacts with formaldehyde to produce glycoaldehyde via a five-center six-electron transition state, and subsequently with the glycoaldehyde to produce glyceraldehyde. Theoretically, four, five and six carbon sugars should be produced in the reactions of water vapor with carbon vapor generated by a high intensity arc. Therefore, the reactions of arc generated atomic carbon and water were performed with the goal of determining which four, five, and six carbon aldose sugars were produced. In addition to glycoaldehyde and glyceraldehyde, the four carbon aldoses erythrose and threose were produced in measurable quantities. The five carbon aldoses arabinose, lyxose, ribose, and xylose were produced in trace amounts.

Because formaldehyde is the product of rearrangement of hydroxymethylene and a potential rate determining step in the production of higher order sugars the reactions of atomic carbon

with water and formaldehyde were performed. Should the reaction of carbon with water proceed via a hydroxymethylene intermediate there should be an increase in the yield of four, five and six carbon sugars. Reactions of atomic carbon with deuterium oxide, and formaldehyde plus deuterium oxide were performed as a verification of the proposed mechanism. The mechanism of hydroxymethylene addition to aldose sugars was discussed.

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LIST OF ABBREVIATIONS

Å	Angstrom
A	Ampere
°C	Degrees Celsius
cm^{-1}	Reciprocal Centimeters
et. al	And Others
F	Fragment Ion
ft	Foot
g	gram
GC	Gas Chromatography
∂	Gamma Particle
ΔH	Enthalpy
ΔH_f	Heat of Formation
^1H NMR	Proton Nuclear Magnetic Resonance
IR	Infrared
hv	Photon(s)
°K	Degrees Kelvin
kcal/mol	Kilocalorie per mole
l	Liter
m	meter
M	Parent Ion
m/e	Molecular Ion
MHz	Megahertz

min	minute
mm	Millimeter
mol	Mole
mmol	Millimole
ml	Milliliter
mg	Milligram
n	Neutron
Oxime-TMS	Trimethylsilylated Oxime Derivative
p	Proton
psig	Pounds per Square Inch
sec	Second
TMS	Trimethylsilyl Group
$t_{1/2}$	Half-Life
UV	Ultraviolet
±	Activated Complex

Abbreviations and format utilized in this thesis conform to thoses used in the Journal of the American Chemical Society.

I. INTRODUCTION

One of the most intriguing questions that has faced mankind has been the source of the origin of life on Earth. A relatively new field, prebiotic chemistry, has developed in an effort to answer some of the questions of chemical evolution. Recent studies by radioastronomy have shown that there is a large amount of matter between the stars of our galaxy.[1] This matter is located in clouds in the form of spherical shells which appear to be expanding and may be remnants of supernova explosions as previously predicted.[2]

Of the elements thus far identified throughout the universe, the six most abundant are hydrogen, carbon, nitrogen, oxygen, sulfur, and phosphorus. These just happen to be the ones necessary for the formation of organic compounds. Indeed, in 1968, formaldehyde became the first organic molecule to be found in interstellar space. Since then, corresponding to the development of radiotelescopes, over fifty molecules have been discovered in interstellar space using microwave spectroscopy. Interestingly, the first five organic molecules detected in different regions of the galaxy are among the most important for prebiological synthesis of organic compounds: Ammonia (NH_3), a basic catalyst as well as a source of amino groups; water (H_2O), the universal solvent; formaldehyde (CH_2O), the precursor of carbohydrates; hydrogen cyanide (HCN), the precursor of both amino acids and

purines; and cyanoacetylene (HC_2CN), the precursor of the pyrimidines. The complexity of the molecules detected to date ranges from diatoms (like CO) to polyatomics (such as cyanotetraacetylene). Some of these molecules have also been found in comets, and the Jovian planets and their satellites.

Surprisingly, the Earth does not contain large amounts of organogenic elements (H, C, N, O, S, and P) in proportion to other elements. However, obviously there are enough organogenic elements for organic synthesis. Current theory ascertains that the organogenic elements became part of the atmosphere and hydrosphere by a process of outgassing during the early accretion period of the earth. And potentially, additional quantities of these elements were incorporated in the Earth's atmosphere by capture of comets and carbonaceous chondrites during the late accretion phase.[3] Comets are known to be made of ices of water mixed with organic and inorganic compounds, and carbonaceous chondrites contain amino acids and other compounds. Two examples of these most likely sources of prebiotic compounds are two meteorites; the Murchison which fell in Australia in 1969, and the Alan Hills which fell in Antartica in 1953.[4]

The matter resulting from outgassing and late accretion was probably composed of simple gas molecules such as CO_2, CO, N_2, H_2O, H_2S and smaller amounts of H_2, NH_3, CH_4 and possibly other simple organic molecules such as those found in interstellar space, comets, and carbonaceous chondrites.[5]

The synthesis of organic and biochemical compounds apparently occurred on the primitive Earth in at least two major phases: the formation of biochemical monomers followed by condensation of

monomers into oligomers and polymers. This premise has become the cornerstone of prebiotic chemistry.

The feasibility of performing simple laboratory experiments to study the origins of life was first reported by Stanley Miller, in 1953, when he successfully produced amino acids from a mixture of methane, ammonia, hydrogen and water vapor by passing an electric discharge through it.[6] Since then a multitude of experiments have demonstrated the formation of amino acids and other organic compounds by subjecting simulated primative Earth atmospheres to a variety of energy sources. Prebiotic synthesis of carbohydrates probably involved formaldehyde as a reacting species. Prebiotic formaldehyde in turn had to result from the combination of atomic carbon, hydrogen, and oxygen or more likely the combination of atomic carbon and water. Therefore, efforts to simulate conditions for the prebiotic synthesis of carbohydrates in the laboratory should entail generation of atomic carbon in the presence of water and/or formaldehyde, and provision of a cold surface for condensation reactions to occur.

Preparation and Reactions of Atomic Carbon

Atomic carbon is one of the most energetic intermediates in chemistry possessing three low lying electronic states.[7] The ^3P ground state has a heat of formation of 171 kcal/mol, while two low-lying metestable singlets, C(^1D) and C(^1S), have ΔH_f of 201 and 233 kcal/mol, respectively.[8] This high potential energy is like a two sided coin; it makes generation of atomic carbon difficult however, it also causes atomic carbon to be highly reactive.

Production of Atomic Carbon

Thus far, experiments designed to produce atomic carbon have followed one of two generalized patterns. One has either injected sufficient energy into a system to convert a precursor to carbon atoms, or a precursor with sufficient internal energy for decomposition to carbon atoms has been used as starting material.

Nuclear Recoil Methods

Nuclear reactions have been utilized to prepare radioactively labeled carbon atoms, either ^{11}C or ^{14}C. These methods involve the bombardment of a host molecule with a high energy atomic particle. Recoil of the highly energetic radioactive carbon results in bond breaking and the production of a free carbon atom. Some examples of nuclear reactions that have been utilized are: $^{14}N(n,p)^{14}C$,[9] $^{12}C(n,2n)^{11}C$,[10] $^{12}C(p,pn)^{11}C$,[11] $^{10}B(d,n)^{11}C$,[12] $^{11}B(p,n)^{11}C$,[12] $^{12}C(\partial,n)^{11}C$,[13] and $^{14}N(p,\partial)^{11}C$.[14] The radioactive carbon atoms produced by nuclear reactions are born at 4500 kev and lose their energy through elastic and inelastic collisions and are thought to react either in their ^3P ground state or in one of the lower energy metastable singlet (^1D or ^1S) states. The entire excess kinetic energy these atoms possessed may not be dissipated prior to reaction, thus making reactions of hot carbon atoms a significant factor in these systems. The yield of carbon atoms is relatively low ($\approx 10^7$ atoms) and product analysis must be performed by radiochemical techniques. The products are usually analyzed by radiochromatography and identified by the half-life of ^{11}C ($t_{1/2}$=20.4 min) and ^{14}C ($t_{1/2}$= 5770 yrs). A major disadvantage of this method is that only products containing the radioactive

carbon are detected. However, this is offset by the fact that the atomic carbon produced is 100 percent C_1.

Graphite Vaporization Techniques

The Carbon Arc. The carbon arc method of generating atomic carbon has been pioneered by P. S. Skell and his coworkers.[15] Carbon vapor is produced in an arc between two graphite electrodes and cocondensed on a liquid nitrogen cooled surface with an excess of substrate. The carbon atoms are produced at high temperature (≈2500°C) in a low pressure (≈$5x10^{-5}$ torr) atmosphere and travel less than one mean free path during the flight to the cool walls (-196°C). This minimizes the probability of gas phase reactions between carbon atoms and substrate during flight and reactions are believed to occur in the condensed phase although the exact temperature of reaction is not known. Carbon atoms are produced in high yields and in all three low lying energy states. In addition, C_1, C_2, C_3, and C_4 are produced in the carbon arc in the ratio of 100: 35-48: 7-10: 0.6-1.0.[16] Reactions of these species must be taken into account when interpreting the results of an experiment with arc-generated carbon. Also, pyrolysis of products formed in the immediate vicinity of the carbon arc and potential photolysis products as a result of ultra violet(UV) radiation must be considered.

Heating of Graphite. Graphite heating results in the evaporation of carbon from graphite. Usually the graphite is resistively heated to an excess of 2200°C and the evaporated vapor is allowed to react with substrate.[16,17] The relative amounts of C_1, C_2, and C_3 in graphite vapor have been determined by mass spectroscopy[18] and by chlorine trapping experiments.[19] The vapor

composition depends on the temperature, but C_1 predominates, along with C_2 and C_3. Product studies have shown that only ground state ^3P of C_1 and the singlet states of C_2 and C_3 are available for reaction.[16] Lasers have also been used to generate graphite vapor.[20,21] It is interesting to note that vapor compositions are somewhat different than those of resistively heated graphite with a ratio of $C_1:C_2:C_3$ of 1:1.4:17.[22] Laser heating of tantalum carbide produces carbon vapor with a higher percentage of C_1 as compared to vapor obtained from heating pure graphite.[22]

Photochemical Production of Atomic Carbon

Photolysis of Carbon Suboxide. The photolysis of carbon suboxide has been studied extensively and is exemplified by equations (1)-(3).[23]

$$O{=}C{=}C{=}C{=}O \xrightarrow{h\nu} [:C{=}C{=}O]^* + CO \qquad (1)$$

$$[:C{=}C{=}O]^* \longrightarrow :C: + CO \qquad (2)$$

$$[:C{=}C{=}O]^* \longrightarrow C_2 + O \qquad (3)$$

A pioneering UV absorption study of the flash photolysis of carbon suboxide at 1590 Å revealed that carbon atoms were produced in the ^3P, ^1S, and ^1D electronic states.[23] This study also enabled the measurement of rate constants for the reaction of $C(^3P)$ and $C(^1D)$ with simple substrates.

Photochemical Production of Atomic Carbon in Low Temperature Matrices. Photolysis of cyanogen azide in a matrix at 14°K produced carbon atoms via the following sequence depicted in equations (4) and (5).[24]

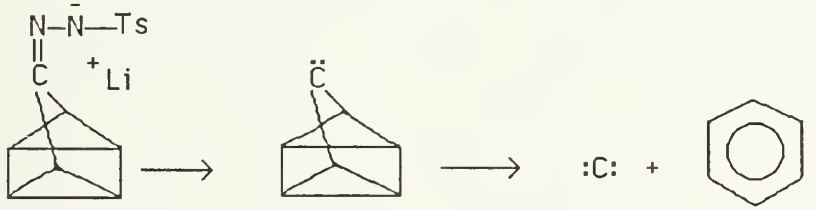
$$N_3{-}C{\equiv}N \xrightarrow{h\nu} N_2 + NCN \qquad (4)$$

$$N{-}C{\equiv}N \xrightarrow{h\nu} :C: + N_2 \qquad (5)$$

The carbon atoms produced are in the ground state, C(^3P) and diffuse through the matrix in order to react with substrates.

Chemical Production of Atomic Carbon

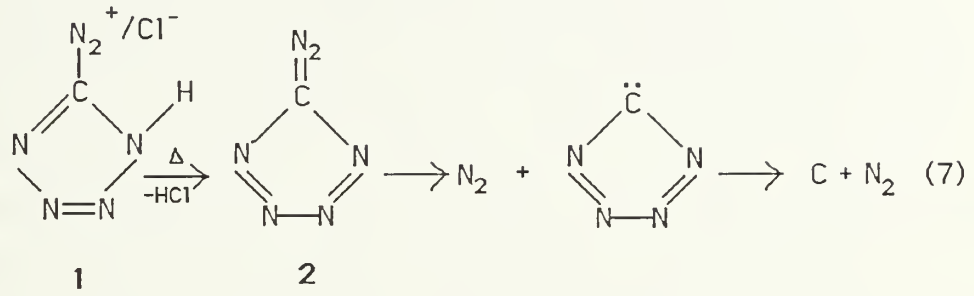
Precursor molecules for the production of carbon atoms must contain sufficient energy such that their decompositions will be spontaneous.One example of such an energy-rich molecule is the carbene, a divalent carbon species, tetracyclo-[3.2.$0^{2,7}$.$0^{4,6}$]-heptane-3-ylidene depicted in equation (6). This compound arises from the pyrolysis of the tosylhydrazone lithium salt as an intermediate in the production of atomic carbon and benzene.[25] The atomic carbon then reacts with benzene to produce toluene.



(6)

Another molecule, the potentially explosive 5-tetrazoyldiazonium chloride, **1**, serves as a precursor to 5-diazotetrazole, **2**, which undegoes thermal decomposition to produce atomic carbon.[26] Reactions of atomic carbon are conducted by performing the pyrolysis of this compound at 100°C in the presence of a gaseous reactant. The carbon atoms are formed at approximately 100°C and possess little excess kinetic energy. It is possisble that atomic carbon is not the actual reactive species in the decomposition of **2**. Although the products resulting from such reactions are the same as those resulting from other methods of atomic carbon

production, the product yields are lower and could invlove the reaction of a carbon atom donor such as CNN.



1 2

Miscellaneous Methods of Atomic Carbon Production

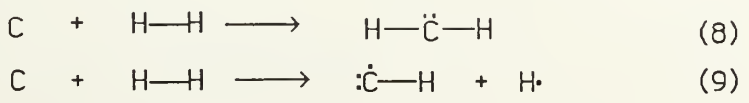
In addition to the methods discussed above, a variety of fascinationg ways of producing carbon atoms have been devised by chemists and warrant mention. Atomic carbon has been produced by passing carbon suboxide or carbon monoxide through a microwave discharge,[27] by the explosion of graphite filaments,[28] through shock tube decompositions,[29] pulse radiolysis,[30] and by the neutralization of a stream of carbon ions.[31]

Reactions of Atomic Carbon

As previously stated, atomic carbon is one of the most fascinating intermediates in organic chemistry. Its high energy makes it extremely reactive and its zerovalent character causes it to behave much like a carbene participating in addition, insertion and abstraction reactions.

Reaction of Atomic Carbon with Hydrogen

Atomic carbon can react with hydrogen by either insertion or abstraction.

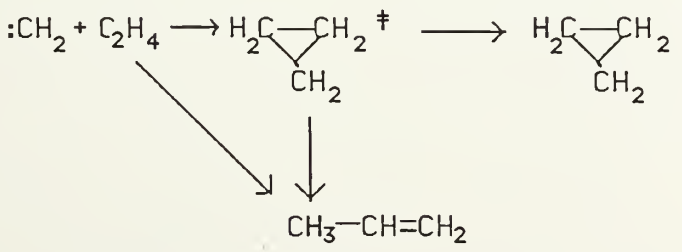


Insertion into the C-H bond to give methylene is exothermic for all three atomic carbon energy states. However, insertion by $C(^3P)$ is expected to be reversible unless stabilization by a third body occurs. Abstraction to yield C-H and H is exothermic for the ^1D ($\Delta H = -6$ kcal/mol) and ^1S states ($\Delta H = -38$ kcal/mol) but endothermic for the ^3P state ($\Delta H = 23$ kcal/mol). Product studies of gas phase reactions of atomic carbon with hydrogen have indicated that a major product is acetylene, particularly in reactions involving laser evporation of graphite[20] and explosion of graphite filament[28]. The mechanism proposed to explain this result involves an abstraction of hydrogen to produce methyne which then dimerizes [equations (10) and (11)]. However, a series of abstractions by C_2 is also consistent with this data.

$$C + H_2 \longrightarrow :\dot{C}H + H\cdot \qquad (10)$$

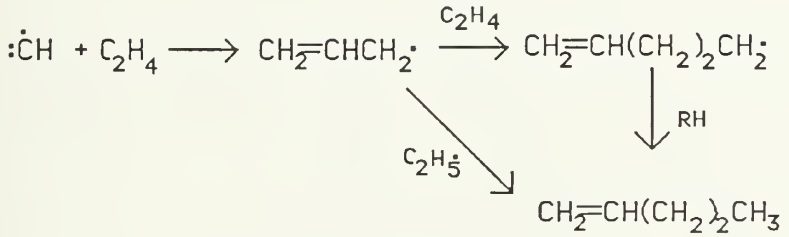
$$2{:}\dot{C}H \longrightarrow H{-}C{\equiv}C{-}H \qquad (11)$$

Reaction of atomic carbon with hydrogen containing five percent ethylene as a trapping agent produced cyclopropane, propylene, and 1-pentene.[32] This indicated that $C(^3P)$ inserts into the H—H bond to produce triplet methylene, which then reacts with ethylene to give cyclopropane or propylene.



(12)

Obtaining 1-pentene as a product has been attributed to the reaction of methyne with ethylene to form an allyl radical which was trapped as 1-pentene [equation (13)]. It was proposed that methyne resulted from decomposition of singlet methylene to methyne and a hydrogen atom in the absence of a stabilizing medium.



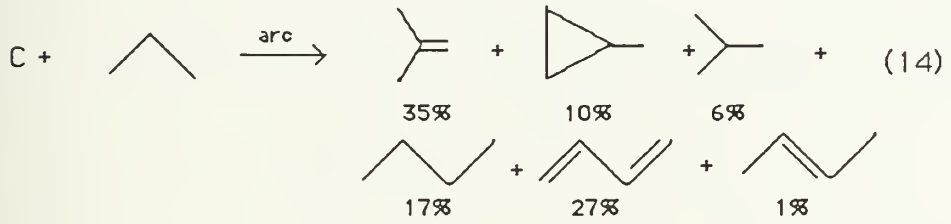
(13)

In contrast to gas phase studies, atomic carbon has been generated by photolysis of C_3O_2 in a matrix at 4°K and reacted with hydrogen to produce methane.[33] The carbon atoms are apparently degraded to their ground state C(^3P) in the matrix and react with hydrogen by insertion to give triplet methylene, which adds an additional hydrogen molecule producing methane. These studies indicate that the behavior of atomic carbon could be summarized as C(^3P) inserts into hydrogen to produce triplet methylene, and C(^1D) reacts with hydrogen primarily by abstraction. This behavior is opposite to that of carbenes, where the singlet inserts and the triplet abstracts.

Reactions of Atomic Carbon with Saturated Hydrocarbons

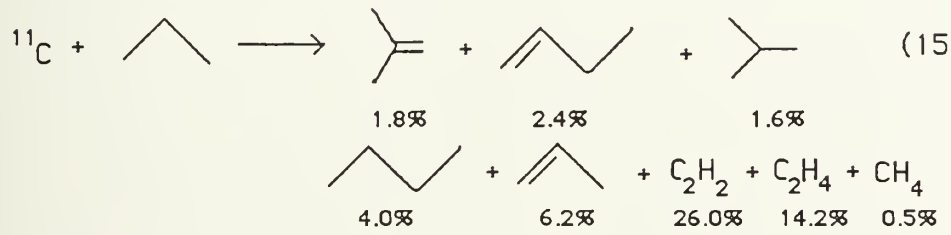
Carbon atoms have been observed to react with hydrocarbons via C-H insertion producing a carbene intermediate,[34] by hydrogen abstraction to generate methyne and a hydrocarbon radical,[35] stripping two hydrogens to form methylene,[36] and by

stripping various larger fragments from the hydrocarbon.[37] No observation of carbon insertion between C-C bonds has been reported. The reaction of atomic carbon with propane has been studied by three methods, and serves as an exempliary reaction of atomic carbon with a hydrocarbon. When arc generated carbon atoms were reacted with propane in the condensed phase at -196°C, the major products were those of equation (14).[38]



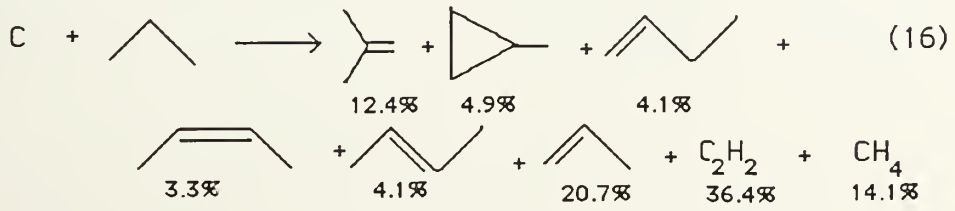
(14)

Equation (15) depicts the products of the reaction of gas phase ^{11}C with propane.[39]



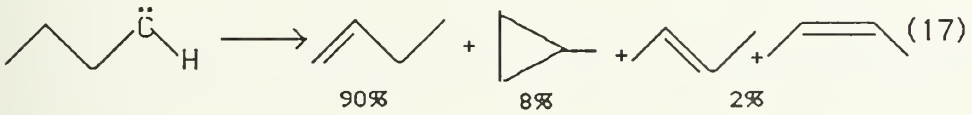
(15)

Equation (16) shows the products that resulted when tetrazoyldiazonium chloride is decomposed in a propane atmosphere.[40]

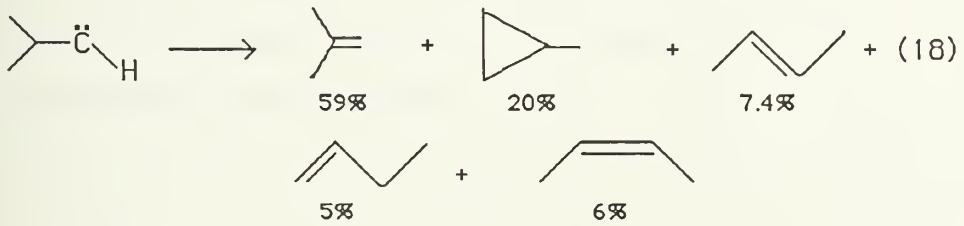


(16)

Analysis of the products of the three reactions show them to be similar although the yields differ considerably. In all cases there are C_4H_8 products of C—H insertion which have been identified as resulting from carbene intermediates as indicated in equations (17) and (18).[41,42]

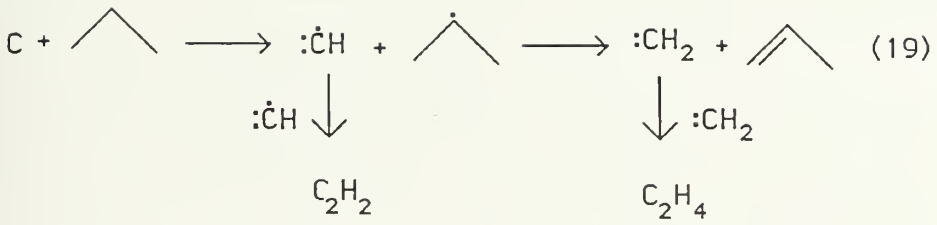


(17)



(18)

The corresponding carbenes were generated in the gas phase by photolysis of the related diazonium compounds. Considering the yields of 1-butene and isobutene in equations (17) and (18) and comparing these to the products of equations (14)-(16), it is apparent that the carbene of equation (18) must predominate in the reactions of atomic carbon with propane. This indicates that in C—H insertion carbon prefers to attack the weaker secondary C—H bonds. The remainder of the products in equations (17) and (18) are formed via rearrangement of the respective carbenes by hydrogen migration, alkyl migration, hydrogen abstraction or insertion. Obviously, the products in equations (14)-(16) cannot all result from from a C—H insertion mechanism. The C_2H_2 and C_2H_4 produced can be accounted for by the following mechanism.

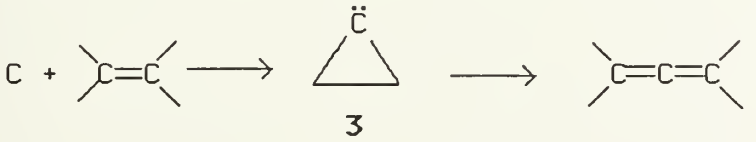


(19)

Lastly, methane production most likely arises from a series of hydrogen abstractions.

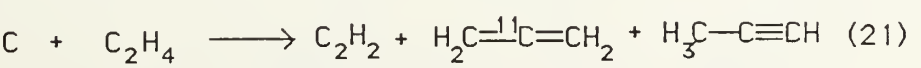
<u>Reaction of Atomic Carbon with Compounds Containing Carbon-Carbon Double Bonds</u>

The presence of unsaturation in substrates adds the possibility of attack at the carbon-carbon double bond to the reprotoire of reactions initiated by atomic carbon. Reaction of atomic carbon with olefins results in the formation of cyclopropylidenes, 3, which are known to undergo unimolecular rearrrangement to cummulenes.[43,44]



(20)

This behavior has also been seen in the reactions of atomic carbon with ethylene, noted by allene and propyne being among the observed products.[45]



(21)

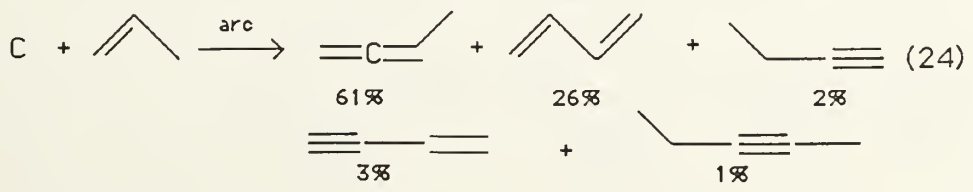
Initially, two mechanisms were proposed which supported the production of allene and propylene, one involving a cyclopropylidene and one involving a vinylcarbene. However, analysis of reactions using ^{11}C revealed that the label predominates on the central carbon of allene indicating that the carbon atom reacts directly with the double bond of ethylene to form a π-bonded species which then rearranges to form allene.[46] These studies also indicated that two mechanisms were in operation in the production of propyne: C-H insertion to generate a vinylcarbene which rearranges to propyne [equation (22)] and rearrangement of an exicted allene to propyne [equation (23)].

$$^{11}C + CH_2{=}CH_2 \longrightarrow CH_2{=}CH{-}{}^{11}\ddot{C}H \longrightarrow CH_3{-}C{\equiv}{}^{11}CH \qquad (22)$$

$$^{11}C + CH_2{=}CH_2 \longrightarrow [CH_2{=}{}^{11}C{=}CH_2]^{\ddagger} \longrightarrow CH_3{-}{}^{11}C{\equiv}CH \qquad (23)$$

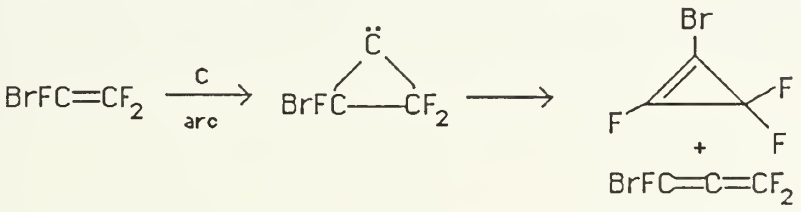
The major process appears to result from addition to the double bond. Supporting evidence for this theory was provided by predominence of the ^{11}C lable on the central carbon.

Addition to the double bond seems to predominate over C-H insertion in the reactions of atomic carbon with simple alkenes. Reaction of carbon with alkenes more complex than ethylene leads to insertion into allylic C-H bonds and subsequent formation of conjugated diens.[47]



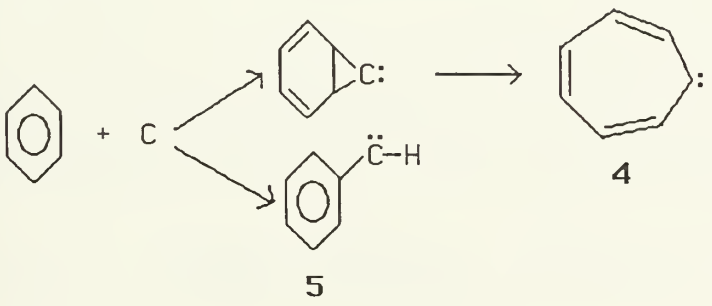
(24)

Additional evidence to support a cyclopropylidene intermediate was obtained when bromotrifluoroethylene was used as the substrate and the kinetically stable cyclopropylidene intermediate was trapped by a bromine migration.[48]



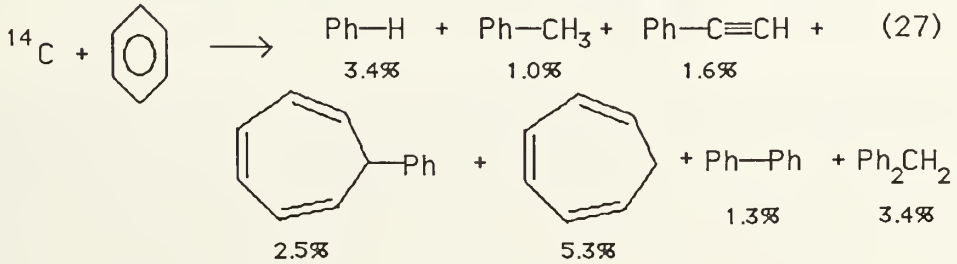
(25)

Reaction of atomic carbon with aromatic compounds has received considerable attention. The reaction of carbon with benzene has been of particular interest. Addition to a double bond should generate cycloheptatrienylidene, **4**, and C-H insertion produces phenyl carbene, **5**.



(26)

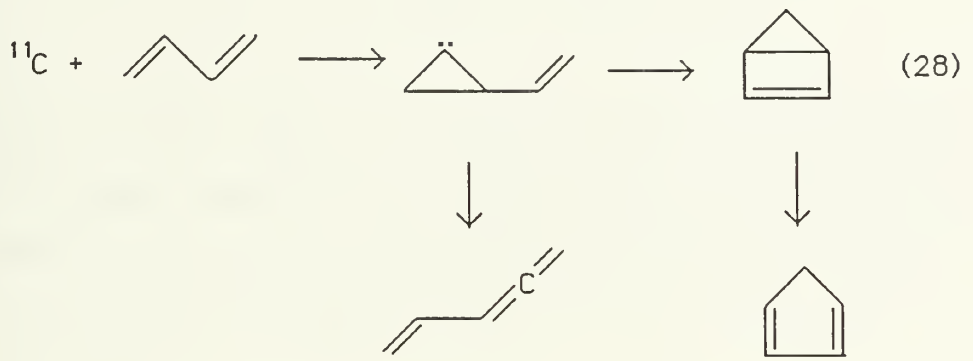
Reaction of ^{14}C with benzene gave the products displayed in equation (27).[49]



(27)

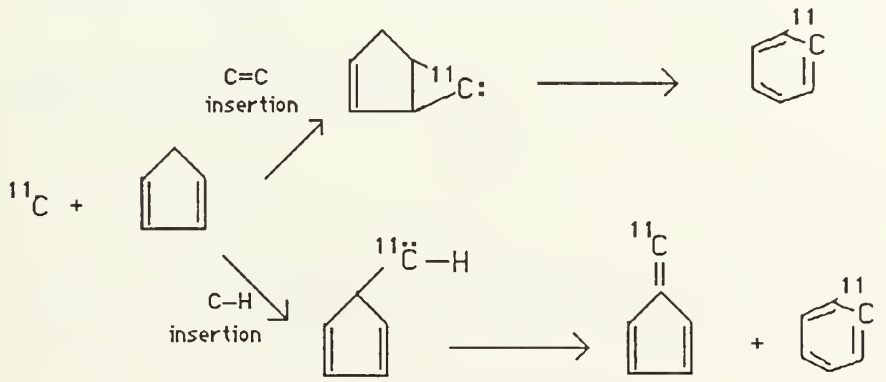
The phenylcycloheptatriene and diphenylmethane have been postulated to result from addition of cycloheptatrienylidene to a second molecule of benzene.

Reaction of atomic carbon, ^{11}C, with 1,3 butadiene gave the products shown in equation (28) via the proposed carbene intermediate.[50]



(28)

Reaction of ^{11}C with cyclopentadiene resulted in benzene and fulvene formation potentially by way of the following mechanism.[51]

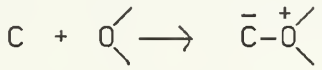


(29)

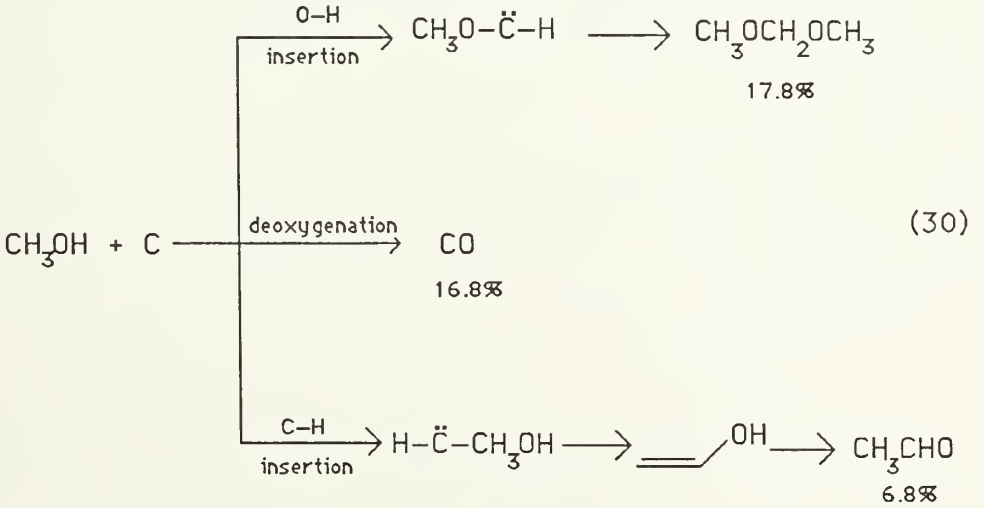
This mechanism clearly indicates that atomic carbon reacts by both C—H insertion as well as double bond insertion.

Reactions of Atomic Carbon with Compounds containing Oxygen and Sulfur

Electrophilic atomic carbon was expected to attack an electronegative atom such as oxygen resulting in the formation of an ylide intermediate in the route to stable products.[52]



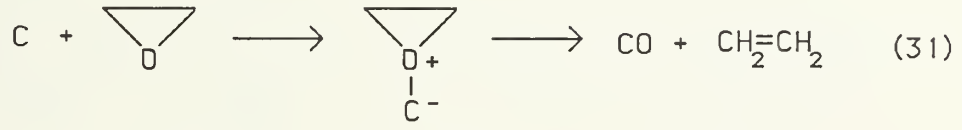
Reaction of atomic carbon with aliphatic alcohols has revealed that the primary reactions are deoxygenation, C—H insertion, and O—H insertion. Reaction of arc generated carbon with methanol gives the products of equation (30).[53]



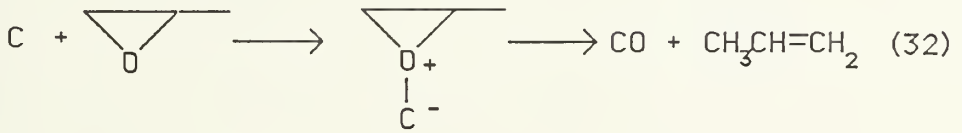
(30)

The proposed mechanism was confirmed by studies using specifically deuterated methanols. These studies also indicated that O—H insertion was found to occur five to eight times faster than C—H insertion. The mechanism for CO production was not elucidated

because the other fragment produced in the deoxygenation was not identified. Deoxygenation also occurs in the reaction of atomic carbon with ethers as indicated by the reactions of equations (31) and (32) involving oxirane and propylene oxide as substrates, respectively.[54,55]

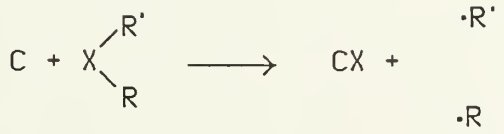


(31)



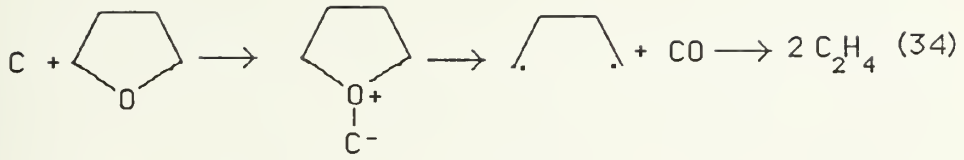
(32)

Comparison studies of deoxygenation and desulfurization have been conducted.[56] The reaction process proceeds by the removal of oxygen or sulfur to generate a pair of radicals as shown in equation (33).

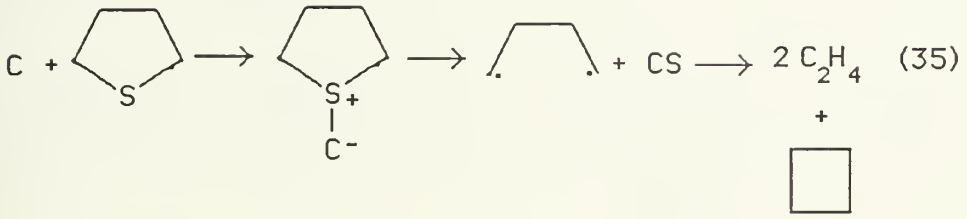


(33)

Because carbon monosulfide possesses more energy than carbon monoxide desulfurizations are less exothermic than deoxygenations. Therefore, desulfurizations usually proceed with less fragmentation and greater stereospecificity than deoxygenations. A comparison study was performed by reacting atomic carbon with tetrahydrofuran and tetrahydrothiophene.



(34)

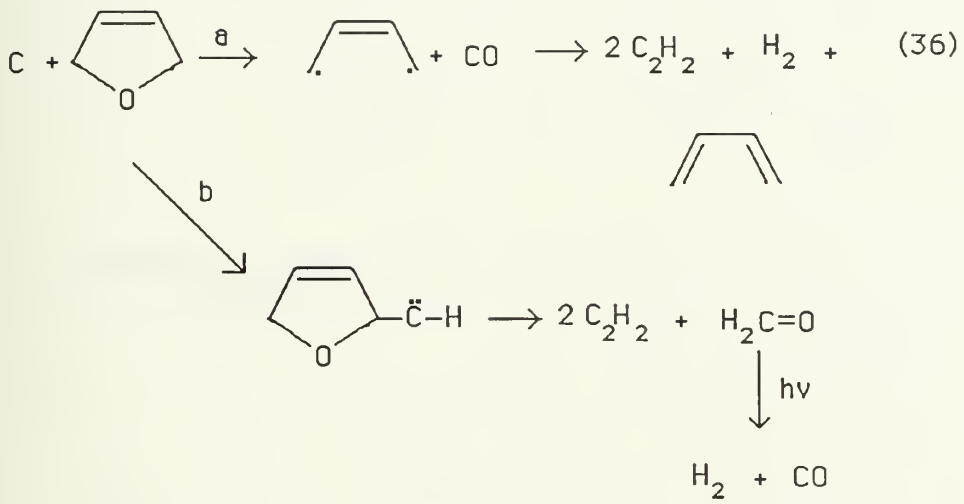


(35)

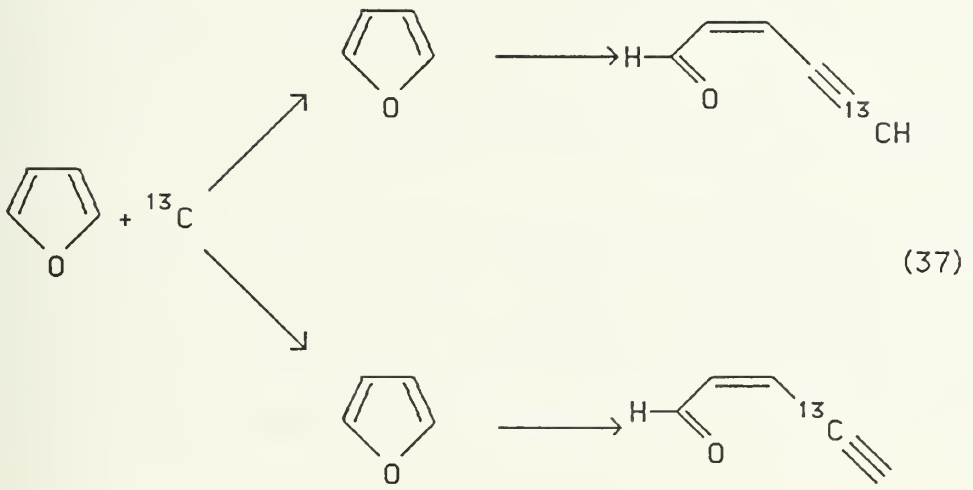
It was observed that the deoxygenation of tetrahydrofuran produced only ethylene which was presumed to arise from cleavage of a tetramethylene biradical. However, desulfurization of tetrahydrothiophene leads to both ethylene and cyclobutane. The presence of the coupling product, cyclobutane, in desulfurization but not from deoxygenation implies that the desulfurization produces a biradical which undergoes less cleavage. Deoxygenation of tetrahydrofuran to biradical and carbon monoxide was found to be exothermic by 122 kcal/mol, while desulfurization of tetrahydrothiophene was exothermic by 63 kcal/mol.[57]

Deoxygenation of 2,5-dihydrofuran yields acetylene in addition to the expected 1,3 butadiene. This reaction was initially postulated to occur according to the mechanism of pathyway (a) of [equation (36)]. This mechanism proposed acetylene formed from biradical cleavage, a reaction which had no precedent in the literature.[56] An alternate mechanism for acetylene formation, pathway (b), was provided by Martino and Shevlin in 1982, in

which the acectylene and some of the carbon monoxide arises from an initial insertion into an allylic C—H bond to generate a carbene intermediate. The carbene then cleaves to yield two molecules of acetylene and formaldehyde. In the carbon arc, a known source of UV light, the formaldehyde photolyzes to carbon monoxide and hydrogen.[58]



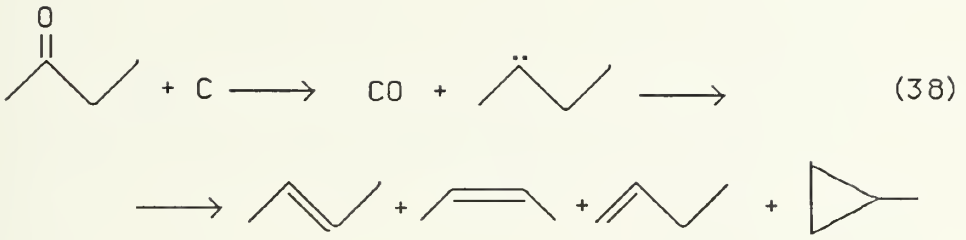
By contrast, deoxygenation did not occur in the reaction of atomic carbon generated by thermolysis of 5-diazotetrazole with gaseous furan.[59] A major product of the reaction was 2-penten-4-ynal as indicated by equation (37).



(37)

The seemingly abnormal behavior of furan was postulated to be a result dictated by the electron distribution in aromatic furan's highest occupied molecular orbital (HOMO) which has no electron density on oxygen.[60] Studies using ^{13}C revealed that the reaction proceeds primarily by insertion into the double bond since the majority of the lable resided on C_4. Therefore, vinylic C—H insertion was only a minor process consistent with the fact that atomic carbon is selective in C—H insertion and prefers the weakest C—H bond.

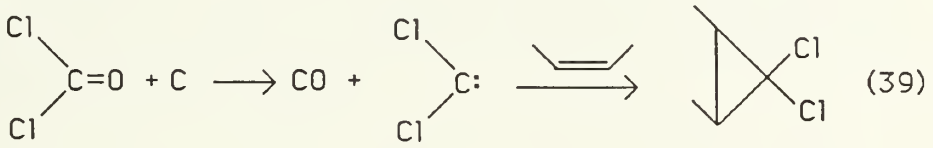
Deoxygenation of carbonyl compounds has been found to be an efficient means of generating carbenes which are difficult or tedious to prepare by other methods.[61] The products formed when 2-butanone was reacted with arc generated carbon are given in equation (38). Methylethylcarbene forms as an intermediate and the resulting products are similar to those formed when the carbene has been generated in other fashions.



(38)

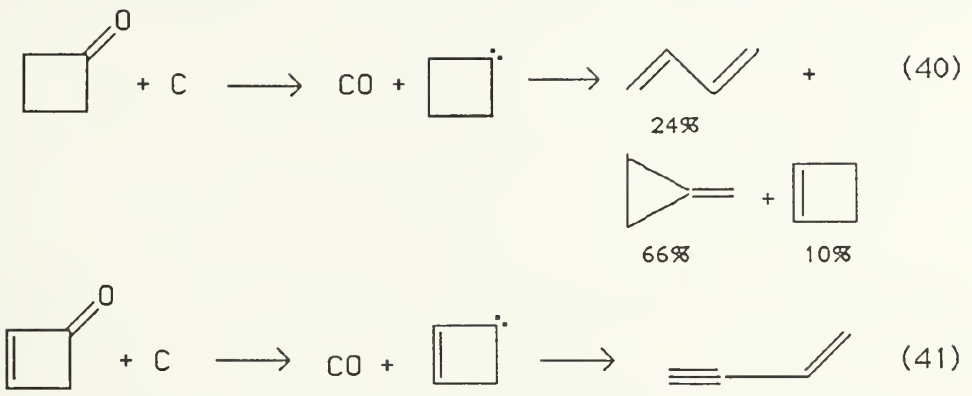
The reacting species in the deoxygenation process was postulated to be either C(^1S) or C(^1D) because of the low yield of carbon monoxide when thermally heated graphite was used as the source of atomic carbon. As previouly stated, thermally heated graphite yields C(^3P) as the primary species.

Deoxygenation of phosgene gives dichlorocarbene which can add stereospecifically to E- and Z- butene. [62]



(39)

Deoxygenation of cyclobutanone gives cyclobutalidene[63] as an intermediate in route to products similar to those reported when cyclobutalidene was prepared from tosylhydrazone [equation (40)].[64] In an analogous reaction, cyclobutenone was deoxygenated to cyclobutenylidene in route to vinylacetylene [equation (41)].[65]

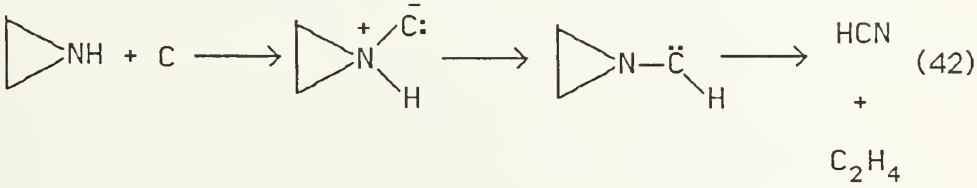


(40)

(41)

Reaction of Atomic Carbon with the Halogens and Nitogen

Aziridines have been observed to react with arc generated carbon to produce alkenes with loss of HCN [equation (42)].[66] When cis-2,3-dimethylaziridine is the substrate, the 2-butenes are produced non-stereoscifically.



(42)

Arc generated carbon reacts with chloronated hydrocarbons to give products attributable to an initial C—Cl insertion.[67] Reaction of carbon tetrachloride and carbon yields tetrachloroethylene and octachloropropane via the mechanism in equation (43).

$$C + Cl\text{-}CCl_3 \longrightarrow Cl\text{-}\ddot{C}\text{-}CCl_3 \longrightarrow Cl_2C{=}CCl_2 \quad (43)$$

90%

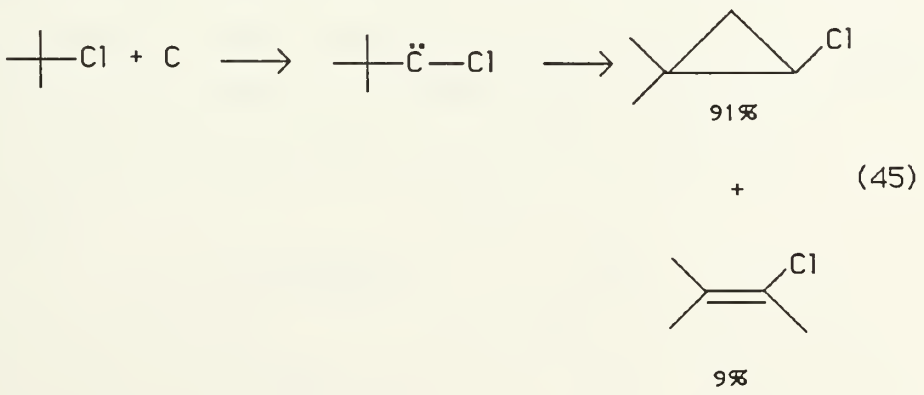
$Cl\text{-}\ddot{C}\text{-}CCl_3 \xrightarrow{CCl_4} Cl_3CCCl_2CCl_3$

10%

Arc generated carbon atoms prefer to insert into the weaker C—Cl bond over insertion into C—H bonds. As an example, 1,1,1-trichloroethane yields 1,1,2—trichloropropene rather than 3,3,3- trichloropropene, a product of C—H insertion. These results support the idea that insertion by atomic carbon is selective towards the weakest bond.

$$C + CH_3CCl_3 \longrightarrow CH_3CCl_2\text{-}\ddot{C}\text{-}Cl \longrightarrow CH_3CCl{=}CCl_2 \quad (44)$$

Alkyl monohalides react with arc generated carbon to give halocarbenes which rearrange to vinyl halides and insert intramolecularly into C—H bonds to produce cyclopropyl halides.[67] This reaction also produces large amounts of acetylene which has been attributed to C—H insertion followed by fragmentation.

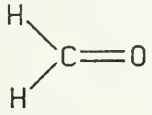


(45)

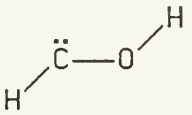
Reaction of atomic carbon with fluorocarbons has been postulated to proceed by fluorine abstraction to yield C–F.[68] Abstraction of fluorine is exothermic by 83 kcal/mol. Reaction of atomic carbon with fluorine in the presence of ethylene has yielded monofluorohydrocarbons.

Formation and Reactions of Hydroxymethylene

Formaldehyde, **6**, is the most stable form of CH_2O, however an alternative structure is that of hydroxymethylene which can exist in either the *trans* or *cis* isomeric form, **7** and **8**.



6



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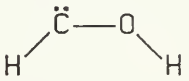
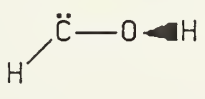
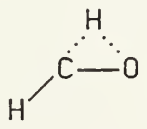


8

Hydroxymethylene has been postulated as an intermediate in several chemical systems and has been the subject of several ab initio calculations.[69-73] However, to date, hydroxymethlene has not been observed spectroscopically in the laboratory. The most recent ab initio calculations, Pople *et al*, 1982, predict the *trans* form of hydroxymethylene to be the most stable isomer, 55.4 kcal above formaldehyde with the *cis* isomer lying 5.0 kcal higher.[69] Interconversion between the *trans* and *cis* forms occurs via internal rotation . The transition structure, **9**, has C_1 symmetry and lies 29.2 kcal above the cis form. The transition structure for the 1,2 shift is the planar form **10**, 84.4 kcal above formaldehyde.



9



10

Hydroxymethylene was initially proposed as an intermediate in the photodissociation of formaldehyde by Buck and coworker's[70] in an attempt to explain a time lag of 4 μs between the decay of the formaldehyde S_1 state and the appearance of the CO photoproduct observed by Houston and Moore [equation (46)].[71]

$$H_2CO(S_0) \xrightarrow{h\nu} H_2CO(S_1) \longrightarrow X \longrightarrow \text{products} \qquad (46)$$

Theoretical work by Lucchese and Scheafer, early in 1978, provided firm evidence that the lowest singlet state of hydroxymethylene lay only 52 kcal above the ground state of formaldehyde. This report was promptly followed by experimental data provided by Sodeau and Lee,[72] which supported the possibility of hydroxymethylene being an intermediate in the photolysis of formaldehyde. They observed glycoaldehyde as the primary product of the mercury arc lamp photolysis of formaldehyde at 12°K in an argon matrix and postulated that it arose from the insertion of a singlet hydroxymethylene into the CH bond of a ground state formaldehyde molecule. They also obseved methanol, CO and H_2 as reaction products and suggested that *cis* -hydroxymethylene might be the precursor to the CO and H_2.

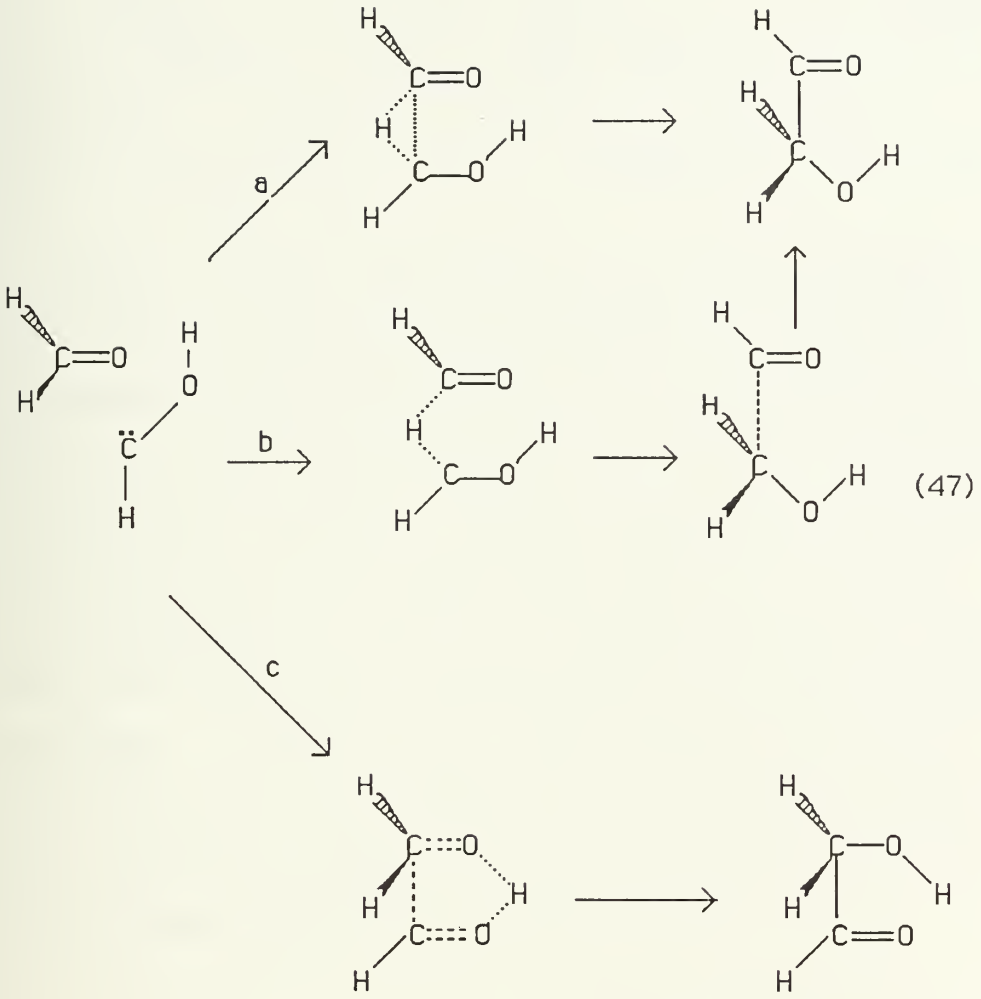
Shortly thereafter, Goddard and Schaefer reported a rather detailed, albeit accurate, theoretical calculation of the photodissociation of formaldehyde at the DZ SCF level.[73] They calculated the *trans* -hydroxymethylene to possess 52.6 kcal/mol more energy than formaldehyde and to be more stable than the *cis* isomer by 5.0-7.7 kcal/mol. The best calculated energy barrier for the rearrangement of formaldehyde to *trans* -hydroxymethylene via a planar transition state was 89 kcal/mol.

By contrast, the barrier to rearrangement of *trans* - hydroxymethylene to formaldehyde was found to be 36.0 kcal/mol. In addition, the barrier to interconversion between the *trans* and *cis* isomers was calculated to be 27.7 kcal/mol. This barrier results from the fact that the CO bond in the hydroxycarbene contains some double bond character evidenced by a CO bond length of 1.337Å which is considerably shorter than the value of 1.437 Å (4-31G SCF) or 1.474 Å (experimental) in methanol.[74] The relaxed rotation involves a transition state with a CO bond length of 1.376 Å at a conformation in which the CH and OH bonds are nearly orthogonal and lengthening the CO bond is associated with destruction of the π bonding between C and O. In 1981, Pau and Hehre measured the enthalpy of formation of *trans* - hydroxymethylene by ion cyclotron double resonance spectroscopy to be 54.2 kcal/mol above formaldehyde a value consistent with calculations.[75]

In 1979, Lee and Diem conducted the photolysis of formaldehyde in an Ar matrix with matrix ratio (M/R) values ranging from 1000 to 10,000.[76] Infrared absorption (IR) spectra of the initial matrix preparations show the matrix isolated monomers are exclusively present at very high dilutiuons (M/R of 5000) whereas cage dimers and higher multimers are present at lower dilutuions. Post photolysis IR spectra indicate that the decomposition of formaldehyde is mainly effected with the cage dimer and that matrix isolated CH_3OH (1033 cm^{-1}) and CO as well as such aggregates as the cage dimers CH_3OH/CO (1040 cm^{-1}) and CH_3OH/H_2CO (1048 cm^{-1}) were photoproducts. No glycoaldehyde was formed in the photolysis of dilute matricies and Lee and Diem

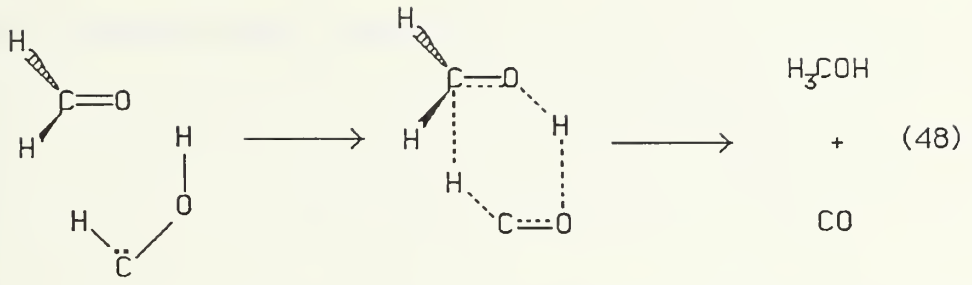
concluded that it is possible that larger concentrations of higher multimers of formaldehyde may play a major role in the formation of glycoaldehyde. Matrix isolated H_2CO present after photolysis appears to indicate the reversible nature of the hydroxymethylene rearrangement in the absence of the matrix reactant.

In 1980, Kemper, Hoeks, and Buck performed ab initio calculations on the reactivity and spectra of formaldehyde isomers and dimeric complexes between them.[77] They concluded that hydroxymethylene was an ambiphilic carbene which forms complexes with formaldehyde that are stabilized by hydrogen bonds. Addition products, glycoaldehyde , methanol and CO, and methyl formate were postulated to arise from a $H_2CO\cdots HCOH$ complexes. Three pathways to glycoaldehyde were considered [equation (47)]. The first two, involving direct C—H insertion and hydrogen abstraction, respectively, were expected from carbene chemistry. In the second mechanism the carbene initially attacks the hydrogen atom, then the two alkyl radicals give C—C bond formation. However, both were eliminated by an energy barrier greater than 60 kcal/mol. Instead, they found that a pathway incorporating a six-electron five-center cyclic transition state possessed the lowest energy barrier 6.37 kcal/mol [pathway c of equation (47)].



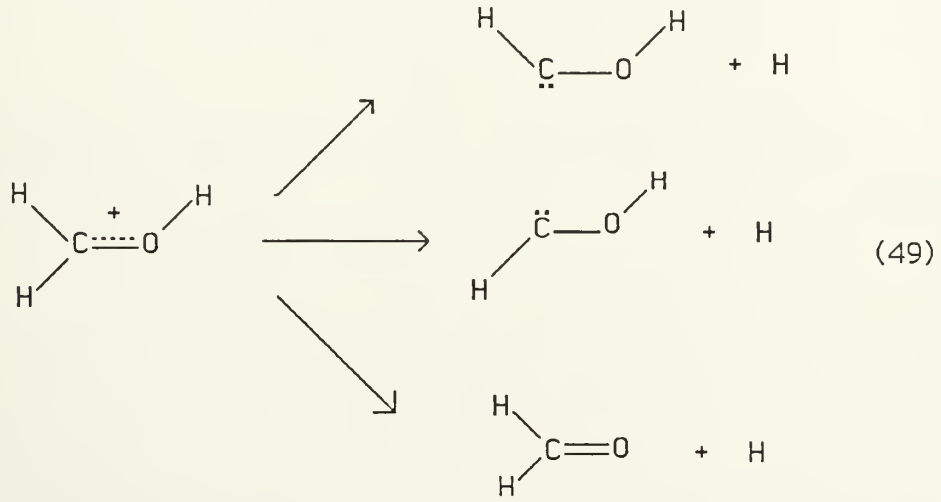
(47)

A similar six-electron cyclic state involving *cis* - hydroxymethylene was found for the production of methanol and CO. Its energy barrier was 10.42 kcal/mol. The barrier to formation of methyl formate by C—H insertion was 35.1 kcal/mol.



(48)

In 1981, Schaefer and Hoffman proposed the statistical argument that hydroxymethylene is twice as likely to be formed via dissociative recombination from H_3CO^+, the lowest energy isomer of protonated formaldehyde [equation (49)].[78] The dissociative recombination process is generally considered important in interstellar clouds and they predict that *cis* and *trans* hydroxymethylene are formed in interstellar clouds via this mechanism. Observance of these species will depend upon their lifetimes. In addition, their detection will depend upon their observance first in the laboratory following the precedent that the interstellar species found to date have been those whose spectroscopic data were well known.

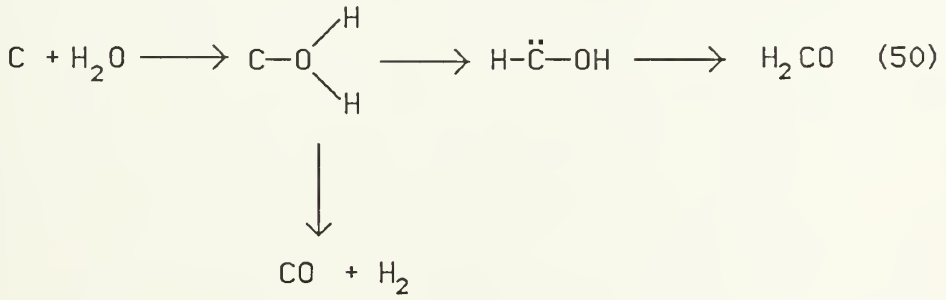


(49)

Reaction of Atomic Carbon with Water

In 1972, Trembly and Kaliaquine reported observation of acetylene, carbon monoxide and hydrogen in the reaction of water with carbon vapor in a high intensity arc reactor.[79] No carbohydrate producion was reported.

However, in 1983, Ahmed, McKee, and Shevlin, reported the results of an experimental and theoretical investigation of the addition of atomic carbon to water.[80] The theoretical study, in which all geometries were optimized at the 3-21G level and single point calculations were performed at the UMP3/6-31G** level, involved both ^1D and ^3P states of carbon. For C(^1D) the process having the lowest activation enthalpy was cleavage of an initially formed carbon water complex to CO and H_2 along a closed shell surface ($\Delta H^{\ddagger}$ = 5.2 kcal/mol).

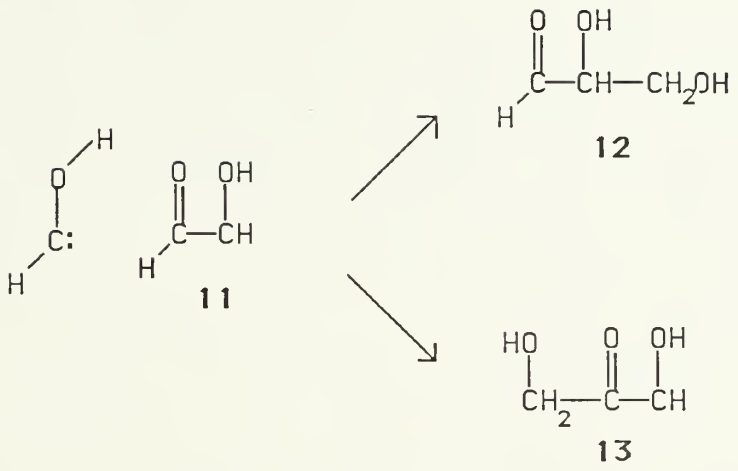


(50)

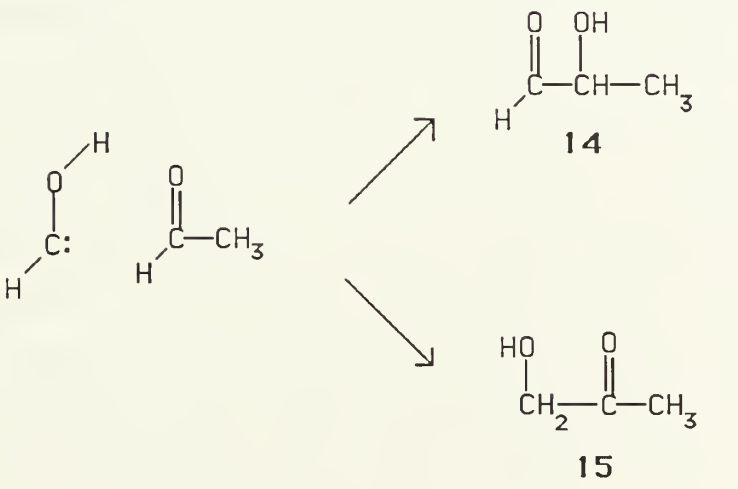
Rearrangement of the closed shell carbon water complex to hydroxymethylene had $\Delta H^{\ddagger}$ = 11.6 kcal/mol. In the case of triplet carbon the most favorable reaction of the initial carbon water complex was dissociation to C and H_2O. The $\Delta H^{\ddagger}$ for the rearrangement of the C(^3P)-H_2O complex to hydroxymethylene was 22.8 kcal/mol while the corresponding barrier for an open shell singlet complex was 18.0 kcal/mol. The barrier to rearrangement of singlet hydroxymethylene to formaldehyde (38.9 kcal/mol) and

that of triplet hydroxymethylene (41.3 kcal/mol) were similar. Experimentally, atomic carbon generated from the thermolysis of 5-diazotetrazole was reacted with water yielding carbon monoxide (9.5%) and formaldehyde (2.4%). Addition of O_2, a scavenger of $C(^3P)$ increases the CO yield to 53.7% while leaving the formaldehyde yield unchanged. Reaction of carbon with O_2 alone produces CO (47%). These results indicate that the state of carbon reactive towards water is a singlet, in concurrence with the calculations.

In 1984, Ahmed, McKee, and Shevlin reported that hydroxymethylene had been produced by the reaction of arc generated carbon atoms with water yielding formaldehyde, glycoaldehyde, **11**, glyceraldehyde, **12**, and dihydroxyacetone, **13**.[81] Deuterium labeled hydroxymethylene reacted with formaldehyde to generate glycoaldehyde which was labled with a deuterium on the aldehydic carbon. This result along with theoretical calculations using MP2/6-31G* indicated that hydroxymethylene reacts with formaldehyde via a five-center transition state involving nucleophilic attack of the carbene carbon on the aldehydic carbon with concurrent transfer of the hydroxyl hydrogen to the carbonyl oxygen. This mechanism is in agreement with that of Buck *et al*, above. Furthermore, theoretical studies of the reaction of hydroxymethylene with glycoaldehyde and acetaldehyde indicate that the five-center transition state predominates in these systems as well. Reaction of hydroxymethylene with glycoaldehyde produces glyceraldehyde and dihydroxyacetone, while the acetaldehyde reaction results in lactaldehyde, **14**, and hydroxyacetone, **15**.



(51)



(52)

In addition generation of hydroxymethylene in the presence of (Z)-2-butene resulted in the formation of butane indicating that hydroxymethylene also behaves as a hydrogen donor.

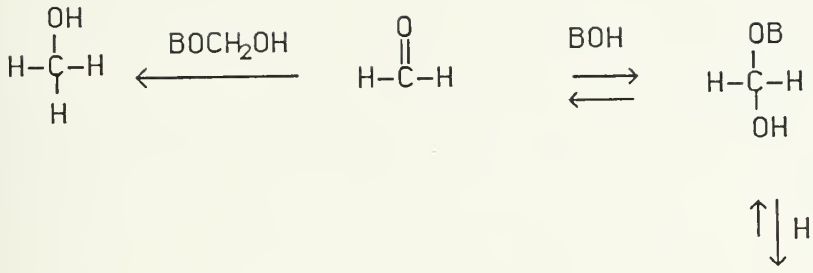
The Formose Reaction

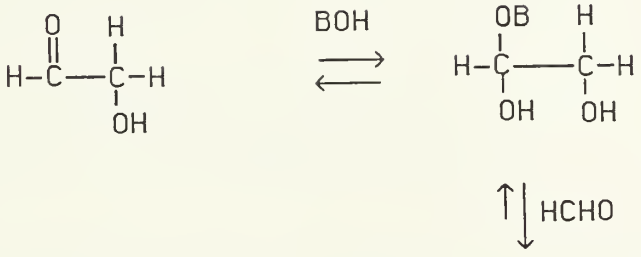
The formose reaction, which produces a complex mixture of sugars and sugar alcohols (the so-called formose) via the base-catalyzed condensation of formaldehyde, is another potential means of prebiotic synthesis of carbohydrates. The formose reaction was first reported by Butlerow in 1861,[82] and has received considerable attention in recent years with regard to the prebiotic synthesis of carbohydrates , the microbial utilization of formose sugars,[83,84] and the possible manufacture of edible carbohydrates from formaldehyde. The reaction proceeds in aqueous solution, and is autocatalytic in nature.

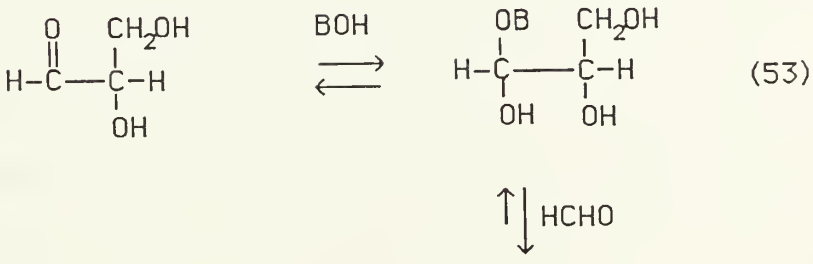
Potentially any base will catalyze the reaction however, the reaction employing calcium hydroxide catalyst in aqueous media has been the most widely investigated. This reaction is thought to proceed in three distinct steps.[85] Initially, an induction period is required for generation of a small amount of condensation products of C_2 and C_3 such as glycoaldehyde, glyceraldehyde, and dihydroxyactone. These species are believed to act as catalytic agents by complexing with calcium ions, in subsequent steps. Formose formation occurs rapidly and the yield of formose sugars reaches a maximum at the so-called yellowing point[86] at which the reaction mixture shows yellow coloration. The third step includes the decomposition of the formed formose sugars under the reaction conditions.

In addition to calcium hydroxide, the formose reaction has been catalyzed by other divalent metal bases, such as barium hydroxides and lead oxides, and by monovalent bases such as thallium hydroxide. [85]

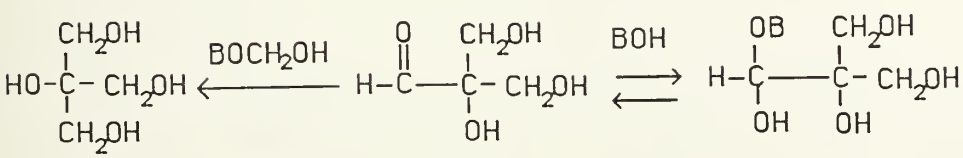
The condensation to sugars occurs in competition with the simple Cannizaro reaction of formaldehyde; the latter course was the sole initial reaction observable when sodium or lithium hydroxides were used.[87] In 1974, Weiss and John proposed $CaOH^+$ as the active catalytic species in $Ca(OH)_2$ catalyzed reactions along with a unifying mechanism for formose and Cannizarro reactions depicted in equation (53).[88]







(53)



Over thirty sugars have been characterized by Mizuno and Weiss as products of the formose reaction.[89] Sugar production has been nonselective for the most part and both branched-chain and straight-chain species have been produced. The toxic formose syrup has been shown to contain aldoses and ketoses ranging from a two carbon product (glycoaldehyde) through three, four-, five-, six-, and seven- carbon, and possibly even higher species, formed by the general process: [87]

$$(n+2)HCHO \xrightarrow{Ca(OH)_2} HOCH_2(CHOH)_nCHO$$

Toxicity of the formose syrup is thought to result from the branched chain and L- sugars which are not metabolized.

Krylov *et al* observed acceleration of the formose reaction and a pronounced shortening of the induction period with the addition of glycoaldehyde and glyceraldehyde, the initial products of the formaldehyde condensation, to the starting mixture.[90] By 1977, it was accepted that the catalitically active species was not the hydroxide of an alkaline earth metal, but its complex with a carbohydrate.[91]

Some selectivity was noted by Shigemasa and coworkers, in 1977, when a high selectivity for a number of sugar alcohols was achieved by removal of most of the dissolved calcium ions at the minimum reaction time as noted by monitoring oxidation-reduction potential changes during the reaction.[85]

In 1980, these workers reported the selective formation of branched chain sugar alcohols achieved by removal of the dissolved calcium ions as hardly soluble salts or stable chelates at the end of the induction period.[92] In 1984, Matsumoto,Yammamoto, and Inoue reported the selective formation of triose (dihydroxyacetone) by the use of thiazolium salts as the catalyst in the formose reaction.[93]

The formose sugars have been studied chromatographically using cellulose column chromatography,[94] paper chromatography[95-97] and gas chromatography of the alditol[98] and sugar[98-100] trimethylsilyl derivatives. These methods of analysis were considered for use in the study of the reactions of atomic carbon with water and higher carbohydrates.

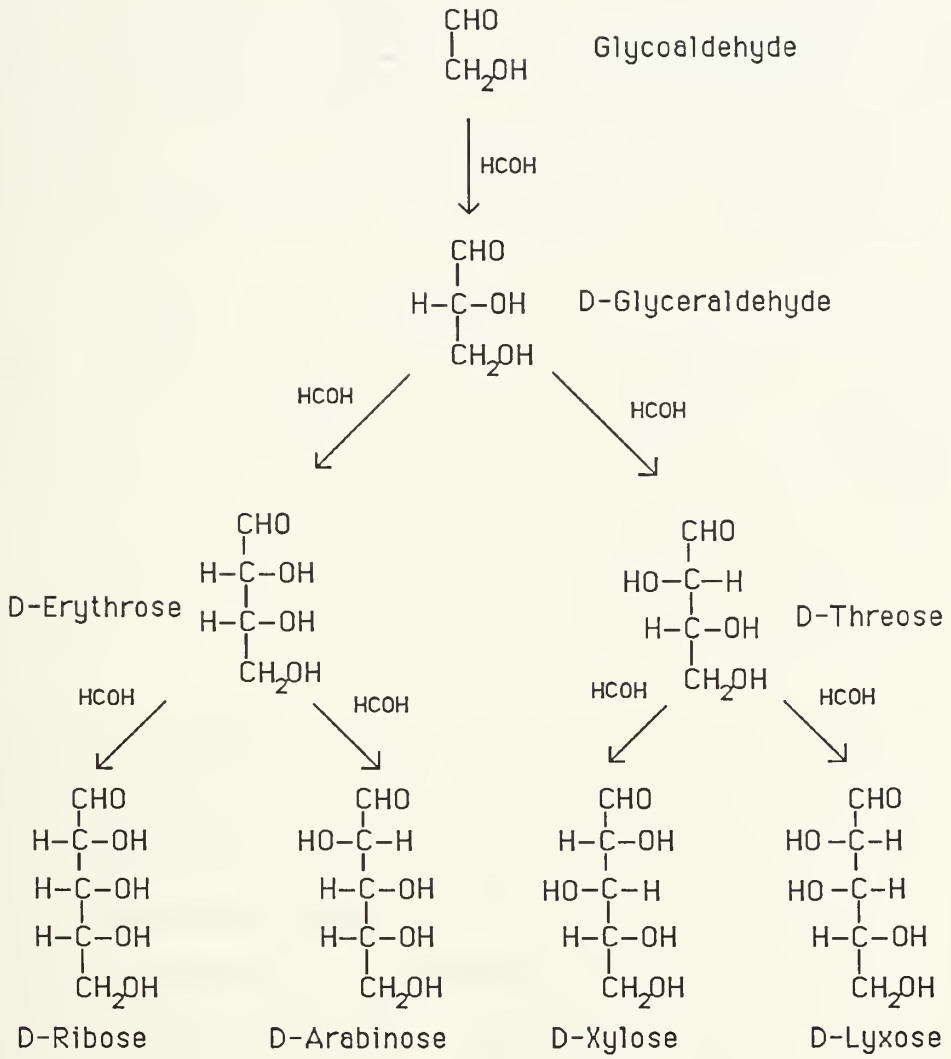
II. RESULTS AND DISCUSSION

Assuming that hydroxymethylene reactcs with higher order carbohydrates as it does with formaldehyde, via a six-electron five-center transition state, a mechanism can be conceived of in which the four carbon sugars; erythrose and threose, the five carbon sugars; arabinose, lyxose, ribose, and xylose, and potentially the six carbon sugars, among these the ubiquitous glucose could be produced (Scheme 1).

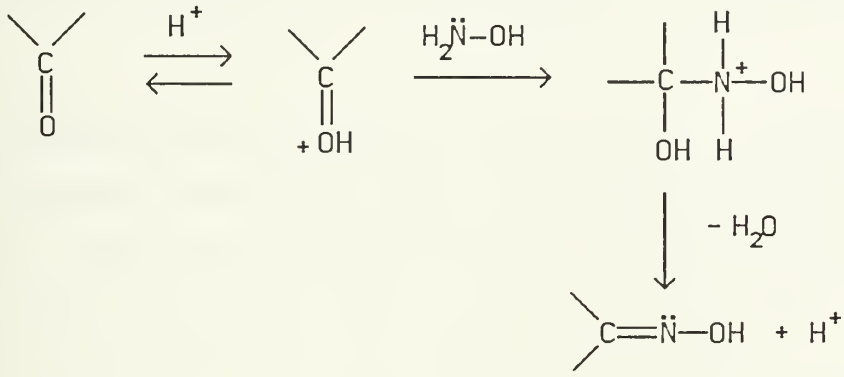
The biological significance of D—ribose and D—glucose stimulated intellectual curiosity and thereby provided the impetus for the major goals of this research. These were to determine which, if any, higher order carbohydrates were produced in the reaction of atomic carbon with water. This information would coincidently provide invaluable clues for the elucidation of one type of reaction of hydroxymethylene.

A complex mixture of carbohydrates, possibly comprised of both sugars and sugar alcohols, was expected from the reaction of atomic carbon with water. Efforts were directed solely towards identification of any aldoses primarily to test the proposed mechanism involving hydroxymethylene addition to the carbonyl group of aldoses via a five-center six-electron transition state as proposed by Ahmed, McKee, and Shevlin.[81]

Scheme 1


CHO
CH2OH
Glycoaldehyde
HCOH
CHO
H–C–OH
CH2OH
D-Glyceraldehyde
HCOH
HCOH
CHO
H–C–OH
H–C–OH
CH2OH
D-Erythrose
CHO
HO–C–H
H–C–OH
CH2OH
D-Threose
HCOH
HCOH
HCOH
HCOH
CHO
H–C–OH
H–C–OH
H–C–OH
CH2OH
D-Ribose
CHO
HO–C–H
H–C–OH
H–C–OH
CH2OH
D-Arabinose
CHO
H–C–OH
HO–C–H
H–C–OH
CH2OH
D-Xylose
CHO
HO–C–H
HO–C–H
H–C–OH
CH2OH
D-Lyxose

The inherent low volatility of sugars rendered conversion of the reaction products to trimethylsilylated oxime (Oxime-TMS) derivatives followed by analysis via gas chromatography and mass spectrometry as the most approriate method for separation and identification of the generated monosaccharides.[101] The general mechanism for oxime formation is represented in equation (54).

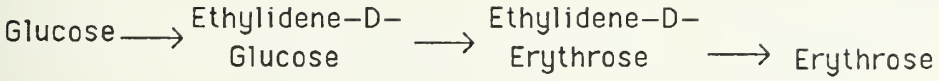


(54)

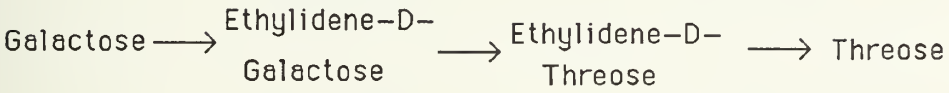
The Finnegan-MAT Ion Trap Detector coupled to a Varian 400 gas chromatograph was utilized extensively during the research. Because of the small concentrations of carbohydrates expected, capillary colums were employed in the gas chromatograph to separate the compounds. The compounds then passed through the Ion Trap Detector which produced a chromatogram and performed mass sprectral analyses by electronic ionization, a technique similar to chemical ionization in a conventional mass spectrometer.

During the course of the research, erythrose and threose were synthesized from glucose and galactose by the following schemes.[102,103]

Scheme 2

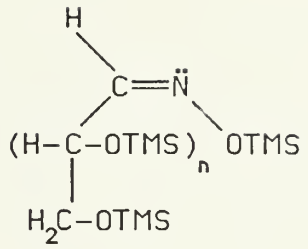


Scheme 3

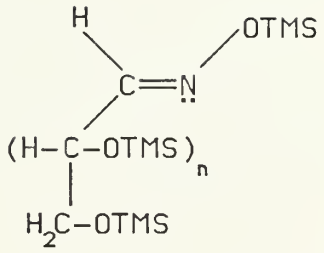


The detailed procedure of the synthesis and the resultant spectroscopic data are provided in the experimental section of the thesis. The proton NMR spectra of the products and intermediates are quite complicated, and the positions of all peaks (ppm) were simply listed with the corresponding intensities.

Standard solutions of the monosaccharides and sugar alcohols were prepared, and portions of these were converted to Oxime-TMS derivatives. The initial analysis were performed on a Charisil-III capillary column which was designed to separate D- and L- amino acids. The majority of the separations were accomplished with a DB-5, 30 m, 0.25 cm i.d., fused silica capillary column. Two peaks were expected in the chromatogram for each sugar because Oxime-TMS derivatives form *syn* and *anti* structures which have different elution times.[104] These structures also possess slightly different mass spectra. The *syn* isomer was expected to be the larger peak because it appears to be more stable from a stereochemical viewpoint with both bulky groups being on the opposite sides of the oxime double bond.

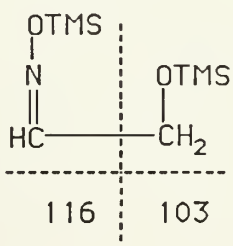


anti

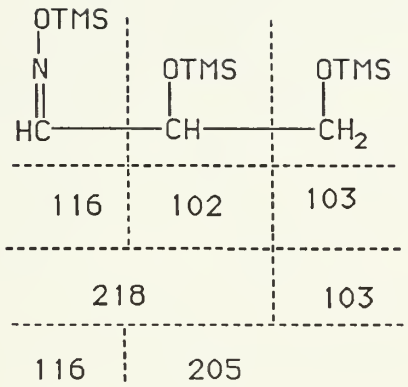


syn

This peak was also expected to show a large M-15 fragment ion in the mass spectra because of the accessibility of the N-OTMS methyl groups to cleavage. Only the D- form of the monosaccharides were utilized in the reseach because of their biological significance. However, potentially four peaks could be observed on the Charasil column because of the presence of L- monosaccharides as an impurity. Expected mass spectral fragmentations were as follows.

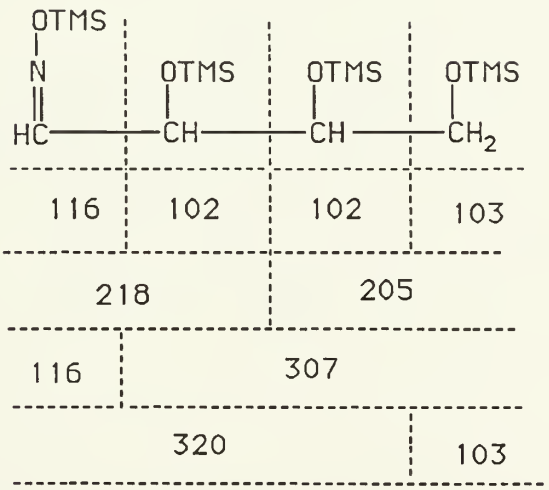
Glycoaldehyde  MW=219

Glyceraldehyde

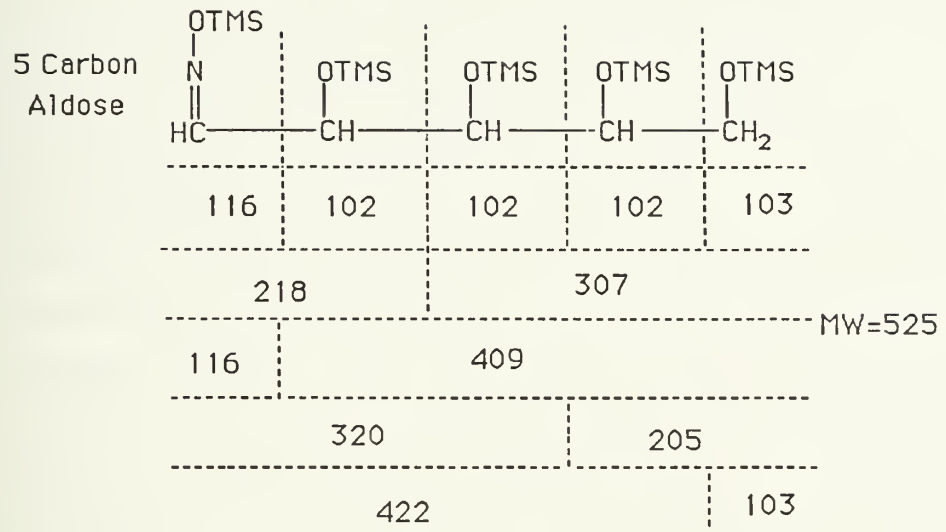


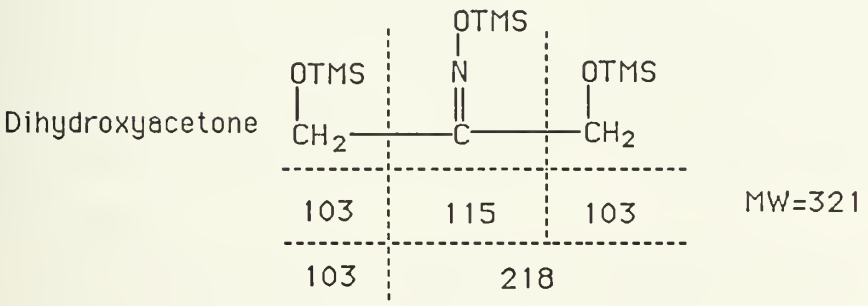
MW=321

4 Carbon Aldose



MW=423





Oxime derivatives were prepared by a method similar to that introduced by Sweeley, Bentley, Makita, and Wells.[101] Hydroxylamine hydrochloride (200 mg) was added to an aqueous solution of either a sugar, sugar alcohol, or reaction products. The sugar alcohols do not form oxime derivatives, but were potential products of a reaction and were therefore derivatized in this fashion for consistency. This solution was heated under vacuum at 80°C for 1-1.5 hours and then evaporated to dryness on

a rotory evaporator. The dried oxime was then dissolved in 1.0 ml pyridine and transferred to a small septum covered vial. The vial was placed under vacuum and the solution was trimethylsilylated by addition of 0.5 ml hexamethyldisilizane and 0.25 ml chlorotrimethylsilane. Trimethylsilylation occured almost immediately and was accompanied by the formation of a white precipitate, ammomium chloride, which gave no interference to subsequent analysis. The contents of vial were then placed under N_2 pressure. The inert atmosphere combined with the excess trimethylsilylating reagents prevented water accumulation and decomposition of the derivatives for periods up to nine months.

The resulting Oxime-TMS derivative was then analyzed by gas chromatography/mass spectroscopy. Because the DB-5 capillary column was employed for separation of the compounds during the majority of the research only retention times and mass spectral data from that source are reported in the experimental section of this thesis.

The typical elution order from the DB-5 capillary column, using a constant temperature of 50°C for one minute follwed by a 5°C per minute heatup rate, is presented in the following tabulation. Detailed gas chromatography/mass spectral data is provided in the experimental section of the thesis.

All Oxime-TMS derivatives were apparently acyclic as evidenced by the presence of two peaks in the chromatogram indicating the formation of both *syn* and *anti* isomers as expected. The first peak eluted usually contained the parent ion (M) or (M+1) as a dominant fragment ion. The second larger peak contained a fragment ion corresponding to the parent ion minus fifteen mass

units (M-15) formed by the well known loss of a silicon linked methyl group.This indicates that the major isomer was *syn* with both bulky groups on opposite sides of the C—N double bond, and it is the second isomer to elute. In addition, the syn isomer shows a tendancy to loose a methyl group and give a M-15 peak in the mass spectra.

Table 1

Elution Order of the Aldose Sugars

Sugar	Peak	Retention Time (sec)	relative
Glycoaldehyde	1	641	0.30699
Glycoaldehyde	2	662	0.31705
Glycoaldehyde	3	679	0.32519
Glyceraldehyde	1	1096	0.52490
Glyceraldehyde	2	1156	0.55364
Dihydroxyacetone	1	1150	0.55077
Erythrose	1	1435	0.68726
Erythrose	2	1451	0.69492
Threose	1	1460	0.69923
Erythrose	3	1486	0.71168
Threose	2	1495	0.71599
Lyxose	1	1744	0.83525
Xylose	1	1750	0.83812
Lyxose	2	1756	0.84099
Xylose	2	1756	0.84099
Arabinose	1	1759	0.84243
Arabinose	2	1764	0.84483
Ribose	1	1787	0.85584
Ribose	2	1790	0.85727
Mannose	1	2050	0.98180
Mannose	2	2088	1.00000

The identification of the particular aldoses was confirmed by the mass spectral data. In addition to the anticipated major ions, some ions were observed which were common to all of the aldoses. Particularly, *m/e* 73 which corresponds to a TMS group and *m/e* 147 which corresponds to a TMS dimer. Other fragments which can be lost are OTMS (*m/e* 89) and trimethylsilanol,

TMSOH,(*m/e* 90). In addition, the fragmented ions (F) were prone to participate in ion molecule reactions, especially with hydrogen ions to give F-1 and F+1. Rearrangements have also been observed to be common in trimethylsilyl ethers of carbohydrates.[105] The major fragment ions are listed below:

Glycoaldehyde:

Peak1: *m/e* 73, 61.40%; *m/e* 103, 84.46%; *m/e* 147, 100%; *m/e* 204, 4.76%; *m/e* 220, 14,54%.

Peak 2: *m/e* 73, 62.76%; *m/e* 103, 100%; *m/e* 147, 68.37%; *m/e* 204, 78.83%; *m/e* 220, 231.17%.

Glyceraldehyde:

Peak 1: *m/e* 73, 74.84%; *m/e* 103, 65.29%; *m/e* 117, 28.34%; *m/e* 147, 30.25%; *m/e* 205, 12.74%; *m/e* 321, 11.15%.

Peak 2: *m/e* 73, 91.39%; *m/e* 103, 57.68%; *m/e* 117, 25.09%; *m/e* 147, 62.55%; *m/e* 205,48.69%; *m/e* 221, 38.20%; *m/e* 306, 84.27%; *m/e* 321, 10.49%; *m/e* 322, 15.73%.

Erythrose:

Peak 1: *m/e* 73, 24.44%; *m/e* 103, 50.00%; *m/e* 117, 68.89%; *m/e* 147, 100%; *m/e* 320, 50.00%; *m/e* 423, 7.78%.

Peak 2: *m/e* 73, 79.41%; *m/e* 103, 100%; *m/e* 117, 61.76%; *m/e* 147, 43.14%; *m/e* 217, 41.18%; *m/e* 320, 7.84%; *m/e* 408, 47.06%.

Threose:

Peak1: *m/e* 73, 58.10%; *m/e* 103, 100%; *m/e* 117, 85.71%; *m/e* 147, 74.29%; *m/e* 217, 52.38%; *m/e* 424, 5.71%.

Peak 2: *m/e* 73, 87.25%; *m/e* 103, 100%; *m/e* 117, 53.92%; *m/e* 147, 50.00%; *m/e* 217, 50.00%; *m/e* 319, 11.76%; *m/e* 408, 77.45%; *m/e* 424, 5.58%.

Arabinose:

Peak 1: *m/e* 73, 22.12%; *m/e* 103, 100%; *m/e* 117, 25.00%; *m/e* 147, 25.00%; *m/e* 217, 9.62%; *m/e* 307, 31.73%; *m/e* 320, 18.27%; *m/e* 510, 8.65%.

Peak 2: *m/e* 73, 9.09%; *m/e* 103, 100%; *m/e* 147, 9.00%; *m/e* 307, 99.00%; *m/e* 320, 42.93%; *m/e* 525, 7.58%.

Lyxose:

Peak 1: *m/e* 73, 10.00%; *m/e* 103, 100%; *m/e* 147, 9.00%; *m/e* 307, 99.00%; *m/e* 320, 77.00%; *m/e* 525, 34.00%.

Peak 2: *m/e* 73, 16.30%; *m/e* 103, 100%; *m/e* 117, 8.89%; *m/e* 147, 18.52%; *m/e* 217, 11.85%; *m/e* 307, 50.37%; *m/e* 320, 38.52%; *m/e* 511, 8.89%; *m/e* 525, 11.85%.

Ribose:

Peak 1: *m/e* 73, 7.94%; *m/e* 103, 100%; *m/e* 117, 4.08%; *m/e* 147, 5.44%; *m/e* 217, 5.90%; *m/e* 307, 19.27%; *m/e* 320, 23.58%; *m/e* 525, 14.06%.

Peak 2: *m/e* 73, 14.91%; *m/e* 103, 100%; *m/e* 117, 10.30%; *m/e* 147, 13.01%; *m/e* 217, 4.61%; *m/e* 307, 7.86%; *m/e* 320, 6.787%; *m/e* 510, 2.71%; *m/e* 525, 2.44%.

Xylose:

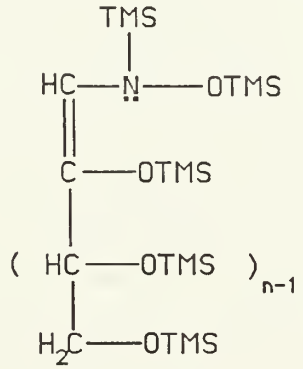
Peak 1: *m/e* 73, 6.43%; *m/e* 103, 100%; *m/e* 117, 3.04%; *m/e* 147, 5.36%; *m/e* 217, 6.25%; *m/e* 307, 6.43%; *m/e* 308, 15.18%; *m/e* 320, 20.71%; *m/e* 525, 6.43%.

Peak 2: *m/e* 73, 13.18%; *m/e* 103, 100%; *m/e* 117, 9.04%; *m/e* 147, 11.89%; *m/e* 217, 4.65%; *m/e* 307, 10.34%; *m/e* 320, 10.34%; *m/e* 510, 8.53%; *m/e* 525, 4.13%.

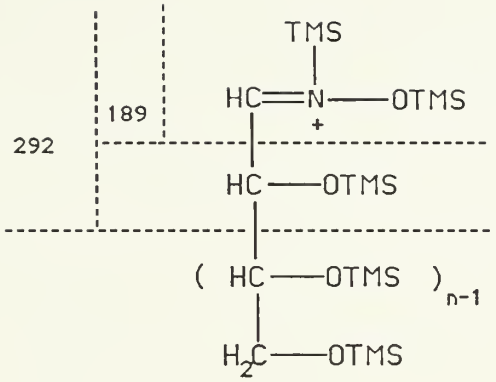
Dihydroxyacetone:

Peak 1: *m/e* 73, 100%; *m/e* 103, 89.99%; *m/e* 114, 1.12%; *m/e* 147, 6.75%; *m/e* 202, 14.33%; *m/e* 203, 6.24%; *m/e* 221, 0.61%; *m/e* 306; 13.21%; *m/e* 321, 2.02%.

Suprisingly, a third peak which possessed a molecular weight of M+73 was occasionally noted in the chromatograms of the Oxime-TMS derivatives. This was particularly true in the case of erythrose and threose. The following structure was proposed as an explanation.



This species most likely results from excess hydroxylamine hydrochloride which acidifies the solution allowing for protonation of the oxime nitrogen. The proton is replaced by a TMS (*m/e* 73) group upon trimethylsilylation . Further evidence supporting the existence of these species were the presence of *m/e* 189 and *m/e* 292 as dominant fragment ions in the mass spectra which correspond to the following fragments.



Analysis of the Oxime-TMS derivatives of the sugar standards revealed that glyceraldehyde and dihydroxyacetone could not be separated. Glyceraldehyde gives two peaks the second of which elutes simultaneously with the lone peak of dihydroxyacetone. Thus glyceraldehyde could be quantitated from the first peak alone. Erythrose and threose could be completely separated even though they possess very similar fragment ions. Erythrose usually eluted in three peaks in the chromatograms of the sugar standard and reaction products. The five carbon aldoses, arabinose, lyxose, and xylose were only partially separable. Ribose was completely separable from the others as it was among the last set of pentose peaks eluted. Usually, only five separate peaks were observed, but separation of these compounds into six and sometimes seven peaks could be achieved by diluting the samples.

Atomic carbon was initially reacted with 1.0 mol of water. The yields from these and other reactions conducted are listed in Table 2, and the mean values along with standard deviations are summarized in Table 3. The actual standardized yields for these reactions were glycoaldehyde (0.0611 ± 0.0194 mmol),

glyceraldehyde (0.0133 ± 0.0064 mmol), erythrose (0.0085 ± 0.0070 mmol), and threose (0.0079 ± 0.0068 mmol) were observed among the reaction products. The amount of dihydroxyacetone was not calculated because of its inseparability from the second peak of glyceraldehyde. The pentoses were present in trace amounts. This was indicated by the presence of small peaks in the chromatogram corresponding to the retention times of the pentoses. But the concentration of the sugars was apparently too low to give totally conclusive mass spectral data in all samples. Major ions noted from mass spectral data of a typical run follow:

Glycoaldehyde

Peak	Retention Time(Sec)
1	653-680
2	685-702

Peak 1: *m/e* 73, 100%; *m/e* 103, 27.21%; *m/e* 115, 1.28%; *m/e* 116, 2.34%; *m/e* 117, 3.35%; *m/e* 147, 28.38%; *m/e* 204, 0.53%; *m/e* 205, 1.60%; *m/e* 219, 0.43%; *m/e* 220, 2.45%; *m/e* 221, 3.41%; *m/e* 222, 0.80%.

Peak 2: *m/e* 73, 100%; *m/e* 103,31.99%; *m/e* 116, 2.71%; *m/e* 117, 1.38%; *m/e* 118, 1.43%; *m/e* 147, 22.08%; *m/e* 204, 23.07%; *m/e* 205, 6.80%; *m/e* 218, 0.74%; *m/e* 219, 0.54%; *m/e* 220, 5.13%; *m/e* 221, 1.18%; *m/e* 222, 0.44%.

Glyceraldehyde

Peak	Retention Time(Sec)
1	1083-1097
2	1135-1164

Peak 1: *m/e* 73, 100%; *m/e* 103, 30.73%; *m/e* 114, 0.56%; *m/e* 117, 5.31%; *m/e* 147, 9.73%; *m/e* 205, 0.72%; *m/e* 218, 0.88%; *m/e* 321, 5.47%; *m/e* 322, 2.49%; *m/e* 323, 0.80%.

Peak 2: *m/e* 73, 100%; *m/e* 103; 24.60%; *m/e* 116, 1.04%; *m/e* 117, 5.98%; *m/e* 118,1.67%; *m/e* 147, 14.51%; *m/e* 218, 1.18%; *m/e* 221, 5.91%; *m/e* 306, 8.13%; *m/e* 321, 3.27%; *m/e* 322, 2.08%.

Erythrose

Peak	Retention Time(Sec)
1	1421-1435
2	1437-1447
3	1470-1480

Peak 1: *m/e* 73, 100%; *m/e* 103, 77.91%; *m/e* 114, 3.41%; *m/e* 115, 3.21%; *m/e* 116, 4.82%; *m/e* 117, 6.63%; *m/e* 118, 2.21%; *m/e* 147, 17.07%; *m/e* 320, 8.23%; *m/e* 336; 1.20%; *m/e* 423, 7.43%; *m/e* 424, 2.61%.

Peak 2: *m/e* 73, 100%; *m/e* 103, 40.58%; *m/e* 117, 34.50%; *m/e* 118, 4.15%; *m/e* 147, 53.67%; *m/e* 205, 7.67%; *m/e* 217, 4.15%; *m/e* 219, 8.95%; *m/e* 320, 7.03%; *m/e* 321, 4.15%.

Peak 3: *m/e* 73, 100%; *m/e* 103, 63.50%; *m/e* 116, 4.10%; *m/e* 117, 11.45%; *m/e* 147, 18.14%; *m/e* 205, 2.38%; *m/e* 320, 16.85%; *m/e* 333, 5.40%; *m/e* 423, 6.26%.

Threose

Peak	Retention Time(Sec)
1	1446-1458
2	1482-1495

Peak 1: *m/e* 73, 100%; *m/e* 103, 63.50%; *m/e* 116, 4.10%; *m/e* 117, 11.45%; *m/e* 147, 18.14%; *m/e* 202, 2.16%; *m/e* 205, 2.38%; *m/e* 320, 16.85%; *m/e* 333, 5.40%; *m/e* 336, 1.30%; *m/e* 423, 6.26%.

Peak 2: *m/e* 73, 100%; *m/e* 103, 15.04%; *m/e* 117, 19.03%; *m/e* 147, 32.08%; *m/e* 217, 1.33%; *m/e* 219, 2.65%; *m/e* 320, 1.99%; *m/e* 408, 2.21%; *m/e* 423, 1.33%.

Pentoses

Peak	Retention Time(Sec)
1	1730-1740
2	1746-1754
3	1755-1763

Peak 1: *m/e* 73, 100%; *m/e* 103, 28.10%; *m/e* 116, 11.90%; *m/e* 117, 22.38%; *m/e* 147, 28.10%; *m/e* 217, 3.33%; *m/e* 224, 2.38%; *m/e* 305, 7.14%; *m/e* 321, 16.19%; *m/e* 347, 9.52%; *m/e* 510, 6.19%; *m/e* 525, 3.81%.

Peak 2: *m/e* 73, 47.69%; *m/e* 103, 100%; *m/e* 116, 1.44%; *m/e* 117, 6.54%; *m/e* 147, 10.05%; *m/e* 217, 10.37%; *m/e* 218, 1.91%; *m/e* 306, 2.23%; *m/e* 307, 15.47%; *m/e* 320, 7.18%; *m/e* 321, 2.87%; *m/e* 510, 13.88%; *m/e* 525, 6.38%.

Peak 3: *m/e* 73, 60.62%; *m/e* 103, 100%; *m/e* 117, 10.20%; *m/e* 147, 14.16%; *m/e* 217, 10.76%; *m/e* 305, 3.68%; *m/e* 306, 2.83%; *m/e* 307, 18.70%; *m/e* 320, 10.20%; *m/e* 525, 3.12%; *m/e* 526, 9.63%.

Table 2

Actual Reaction Yields in mmol Units.

Reactants	Run	Glycoaldehyde	Glyceraldehyde	Erythrose	Threose
C +	1	0.04181	0.02048	0.01005	0.01640
H_2O(20ml)	2	0.06092	0.00845	0.00199	0.00359
	3	0.08066	0.01087	0.00243	0.00189
C +	1	0.04481	0.00763	0.00508	0.00924
H_2O(5ml)	2	0.02809	0.00962	0.00456	0.00449
	3	0.06818	0.00732	0.0381	0.00484
C +	1	0.07917	0.02931	0.00724	0.01070
D_2O	2	0.07017	0.01739	0.01331	0.00615
	3	0.06373	0.01392	0.00331	0.00505
	4	0.04010	0.01546	0.00611	0.00304
	5	0.07323	0.01272	0.00296	0.00396
	6	0.05870	0.01783	0.00403	0.00489
	7	0.06051	0.01272	0.00327	0.00397
C + H_2CO	1	0.06882	0.01316	0.01016	0.00810
+H_2O	2	0.04966	0.00210	—	—
	3	0.00944	0.00207	0.00131	0.00749
C + H_2CO	1	0.02445	0.00328	0.00032	0.00103
+D_2O	2	0.02949	0.01882	0.01014	0.00672

Table 3

Standardized Reaction Yields

Reactants	Glycoaldehyde	Glyceraldehyde	Erythrose	Threose
C + H_2O(20ml)	0.0611±0.0194	0.0133±0.0064	0.0085±0.0070	0.0079±0.0068
C + H_2O(5ml)	0.0470±0.0201	0.0082±0.0012	0.0045±0.0006	0.0062±0.0026
C + D_2O	0.0639±0.0128	0.0170±0.0058	0.0057±0.0037	0.0054±0.0025
C + H_2CO +H_2O	0.0426±0.0303	0.0058±0.0063	0.0057±0.0063	0.0078±0.0004
C + H_2CO +D_2O	0.0270±0.0036	0.0110±0.0110	0.0067±0.0049	0.0039±0.0040
C + H_2O/D_2O	0.0592±0.0161	0.0141±0.0061	0.0053±0.0033	0.0060±0.0039
C + H_2CO +H_2O/D_2O	0.0364±0.0231	0.0079±0.0077	0.0091±0.0042	0.0058±0.0032

In an effort to conduct a realistic analysis of the data the yields of each aldose with respect to glycoaldehyde were calcutated and tabulated in Table 4 for all reactions. The mean values and the standard deviations were calculated and summarized in Table 5. The standardized relative yields for reactions of carbon with 1 mol of water were glycoaldehyde (1.0000), glyceraldehyde (0.2544 ± 0.2039), erythrose (0.1011 ± 0.1207), and threose (0.1583 ± 0.2035).

For a given amount of carbon atoms, larger concentrations of water may promote the formation of hydroxymethylene. Since formation of higher order carbohydrates depends upon hydroxymethylene's rearrangement to formaldehyde and subsequent reaction of the formaldehyde with additional molecules of hydroxymethylene the yields of all aldoses were expected to be higher when compared to yields from reactions employing smaller concentrations of water. In an effort to determine the effect of water concentration on the yield of carbohydrates reactions were performed using 280 mmol of water.

Table 4

Yields of Reaction Products Relative to Glycoaldehyde.

Reactants	Run	Glycoaldehyde	Glyceraldehyde	Erythrose	Threose
C +	1	1.0000	0.48981	0.24037	0.39231
H_2O(20ml)	2	1.0000	0.13868	0.03272	0.05899
	3	1.0000	0.13475	0.03009	0.02348
C +	1	1.0000	0.17034	0.11346	0.20618
H_2O(5ml)	2	1.0000	0.34240	0.16246	0.15974
	3	1.0000	0.10743	0.05594	0.07109
C +	1	1.0000	0.37022	0.09139	0.13511
D_2O	2	1.0000	0.24777	0.18971	0.08771
	3	1.0000	0.21838	0.05194	0.04773
	4	1.0000	0.38560	0.15228	0.09890
	5	1.0000	0.17369	0.04043	0.05415
	6	1.0000	0.30378	0.06870	0.08338
	7	1.0000	0.21016	0.05404	0.06551
C + H_2CO	1	1.0000	0.19130	0.14768	0.11777
$+H_2O$	2	1.0000	0.04223	—	—
	3	1.0000	0.21942	0.13871	0.79355
C + H_2CO	1	1.0000	0.13404	0.01304	0.04199
$+D_2O$	2	1.0000	0.63824	0.34385	0.22789

Table 5

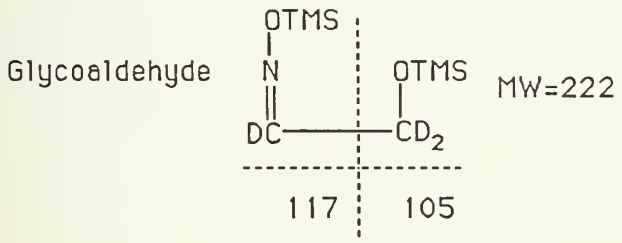
Standardized Relative Yields

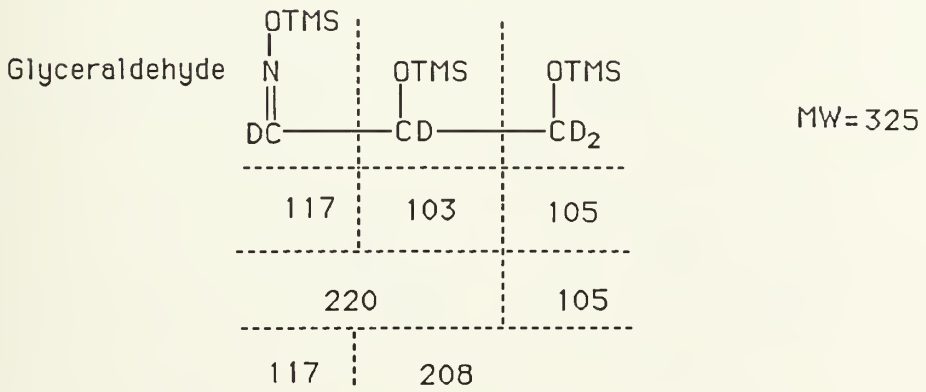
Reactants	Glycoaldehyde	Glyceraldehyde	Erythrose	Threose
C + H_2O(20ml)	1.0000	0.2544±0.2039	0.1011±0.1206	0.1583±0.2035
C + H_2O(5ml)	1.0000	0.2067±0.1216	0.1106±0.0533	0.1457±0.0686
C + D_2O	1.0000	0.2728±0.0822	0.0926±0569	0.0818±0.0299
C + H_2CO +H_2O	1.0000	0.1510±0.0952	0.1432±0.0063	0.4557±0.4778
C + H_2CO +D_2O	1.0000	0.3861±0.3565	0.1784±0.2339	0.1349±0.1314
C + H_2O/D_2O	1.0000	0.2533±0.1163	0.0987±0.0677	0.1142±0.0973
C + H_2CO + H_2O/D_2O	1.0000	0.2450±0.2300	0.1608±0.1366	0.2953±0.3408

In these reactions glycoaldehyde (0.0470 ± 0.0201 mmol), glyceraldehyde (0.0082 ± 0.0012 mmol), erythrose (0.0045 ± 0.0006 mmol), and threose (0.0062 ± 0.0026 mmol) were observed. Small traces of pentoses were present but again only in trace amounts. The yield of carbohydrates did not decrease noticably with the decrease of water concentration, indicating that excess water concentration had no effect on the yield of reaction. The yields of each aldose with respect to glycoaldehyde were very close to those obtained from the reactions using 1 mol of water. These were glycoaldehyde (1.0000), glyceraldehyde (0.2067 ± 0.1216), erythrose (0.1106 ±0.0533), and threose (0.1457 ± 0.0686).

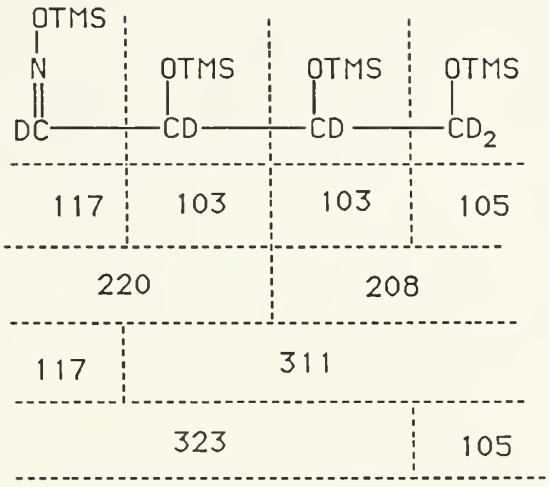
If hydroxylmethylene rearranges to formaldehyde as postulated in the mechanism for aldose formation, then addition of formaldehyde to the reaction mixture should increase the yield of higher order aldoses as compared to yields from the reactions of carbon and water. Reactions of carbon with water, and formaldehyde were performed using 0.3-0.5 g paraformaldehyde which was thermally heated to 120°C to vaporize the formaldehyde into the reactor. The actual standardized yields were glycoaldehyde (0.0426 ±0.0303 mmol), glyceraldehyde (0.0058 ± 0.0064 mmol), erythrose (0.0057 ± 0.0063 mmol), and threose (0.0078 ± 0.0004 mmol). Even though the actual yields appear to decrease the product yields of all aldoses increased relative to glycoaldehyde providing evidence to support the hydroxymethylene's rearrangement to formaldehyde. Subsequent addition of hydroxymethylene formed aldoses. The standardized relative yields were glycoaldehyde (1.0000), glyceraldehyde (0.1510 ± 0.0952), erythrose (0.1432 ± 0.0063), and threose (0.4557 ± 0.4778).

To confirm the the role of hydroxymethylene in the proposed mechanism, reactions of atomic carbon with deuterium oxide were considered. These reactions should produce deuterated hydroxymethylene and subsequently fully deuterated carbohydrates. Although, the retention times of these compounds should be the same as their undeuterated counterparts, the mass spectra of the compounds should be different. Expected mass spectral fragments for the deuterated aldsoses follow:



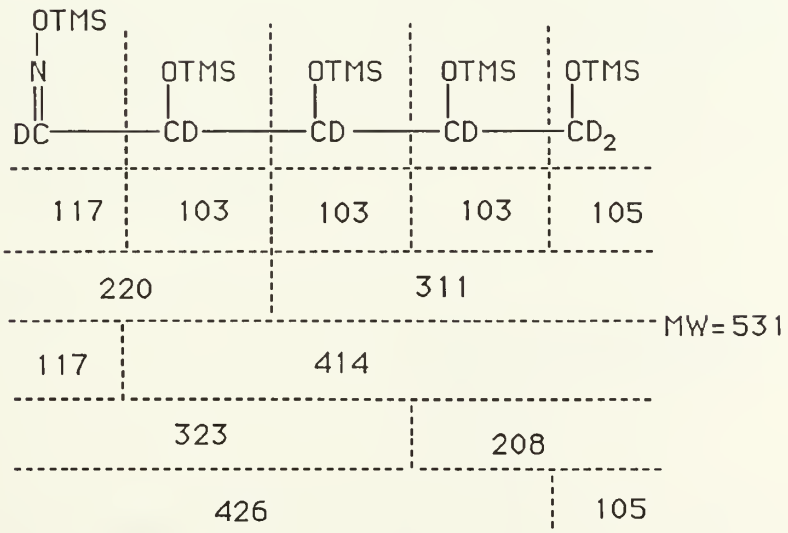


4 Carbon Aldose

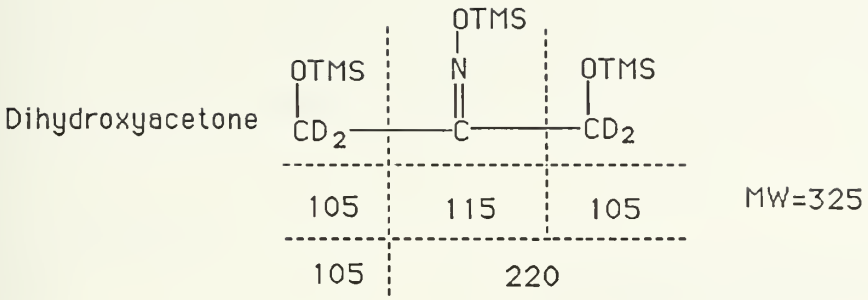


MW= 428

5 Carbon Aldose



MW= 531



Reactions were conducted with 290 mmol deuterium oxide. Fully deuterated glycoaldehyde (0.0639 ± 0.0128 mmol), glyceraldehyde (0.0170 ± 0.0058 mmol), erythrose (0.0057 ± 0.0037 mmol), and threose (0.0054 ± 0.0025 mmol) were observed. Yields with respect to glycoaldehyde were similar to those resulting from the reactions of carbon with water. They were glycoaldehyde (1.0000), glyceraldehyde (0.2728 ± 0.0822), erythrose (0.0926 ± 0.0569), and threose (0.0818 ± 0.0299). Observed mass spectral data from a typical run are listed below.

Glycoaldehyde

Peak	Retention Time(Sec)
1	668-692
2	693-710

Peak 1: *m/e* 73, 100%; *m/e* 103,6.54%; *m/e* 105, 25.76%; *m/e* 117, 3.95%; *m/e* 118, 1.49%; *m/e* 119, 1.49%; *m/e* 147, 34.34%; *m/e* 207, 1.49%; *m/e* 208, 0.78%; *m/e* 221, 2.20%; *m/e* 223, 1.68%; *m/e* 224, 1.88%.

Peak 2: *m/e* 73, 100%; *m/e* 105, 30.02%; *m/e* 116, 1.07%; *m/e* 117, 3.74%; *m/e* 118, 1.53%, *m/e* 119, 1.33%; *m/e* 120, 1.07%; *m/e* 147, 27.69%; *m/e* 207, 22.48%; m/e 208, 4.00%; m/e 209, 1.07%; *m/e* 223, 2.07%; *m/e* 224, 3.47%.

Glyceraldehyde

Peak	Retention Time(Sec)
1	1088-1103
2	1140-1168'

Peak 1:*m/e* 73, 100%; *m/e* 103, 14.99%; *m/e* 105, 28.11%; *m/e* 120, 3.35%; *m/e* 147, 9.64%; *m/e* 202, 1.34%; *m/e* 220,1.47%; *m/e* 325, 8.84%;*m/e* 326,3.48%.

Peak 2: *m/e* 73, 100%; *m/e* 105, 22.92%; *m/e* 119, 0.61%; *m/e* 120, 3.81%; *m/e* 147, 16.87%; *m/e* 202, 0.69%; *m/e* 208, 3.25%; *m/e* 220, 1.56%; *m/e* 221, 5.19%; *m/e* 222, 1.38%; *m/e* 310, 3.20%; *m/e* 325, 1.47; *m/e* 326, 1.90%.

Erythrose

Peak	Retention Time(Sec)
1	1427-1440
2	1443-1449
3	1476-1484

Peak 1: *m/e* 73, 100%; *m/e* 105, 78.87%; *m/e* 116, 4.33%; *m/e* 119, 3.77%; *m/e* 147, 14.44%; *m/e* 204, 2.82%; *m/e* 323,15.14%; *m/e* 324, 3.52%; *m/e* 428, 14.44%; *m/e* 429, 4.58%.

Peak 2: *m/e* 73, 100%; *m/e* 105, 34.25%; *m/e* 120, 27.40%; *m/e* 147, 39.73%; *m/e* 323, 20.55%.

Peak 3: *m/e* 73, 100%; *m/e* 103, 13.64%; *m/e* 105, 19.70%; *m/e* 120, 25.76%; *m/e* 147, 50.76%; *m/e* 323, 7.5%.

Threose

Peak	Retention Time(Sec)
1	1453-1465
2	1488-1497

Peak 1: *m/e* 73, 100%; *m/e* 103, 8.20%; *m/e* 105, 73.77%; *m/e* 116, 9.43%; *m/e* 119, 3.69%; *m/e* 120, 6.15%; *m/e* 147, 24.18%; *m/e* 251, 3.69%; *m/e* 323, 25.41%; *m/e* 324, 5.94%; *m/e* 428, 9.84%.

Peak 2: *m/e* 73, 100%; *m/e* 103, 6.08%; *m/e* 105, 21.55%; *m/e* 120, 16.02%; *m/e* 147, 39.78%; *m/e* 222, 4.42%; *m/e* 323, 10.50%; *m/e* 428, 7.18%.

Pentoses

Peak	Retention Time(Sec)
1	1718-1726
2	1730-1735
3	1737-1747
4	1754-1759
5	1761-1762
6	1764-1768
7	1781-1786

Peak 1: *m/e* 73, 100%; *m/e* 105, 30.56%; *m/e* 147, 25.00%; *m/e* 531, 61.11%.

Peak 2: *m/e* 73, 100%; *m/e* 105, 41.18%; m/e 325, 38.24%.

Peak 3: *m/e* 73, 100%; *m/e* 105, 36.96%; *m/e* 120, 26.09%; *m/e* 147, 50.00%; *m/e* 531, 26.09%.

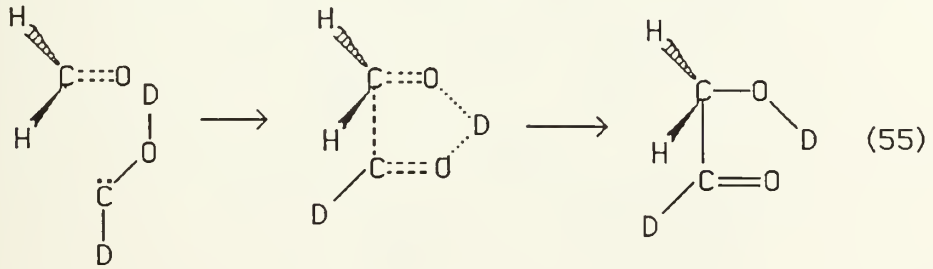
Peak 4: *m/e* 73, 100%; *m/e* 105, 35.79%: *m/e* 147, 25.00%; *m/e* 308, 17.50%.

Peak 5: *m/e* 73, 100%; *m/e* 105, 35.29%; *m/e* 452, 32.35%.

Peak 6: *m/e* 73, 81.25%; *m/e* 75, 100%; *m/e* 103, 68.75%; *m/e* 105, 28.13%; *m/e* 256, 18.75%; *m/e* 331, 15.63%.

Peak 7: *m/e* 73, 73.08%; *m/e* 75, 100%; *m/e* 105, 46.15%; *m/e* 516, 23.08%.

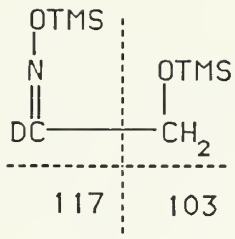
Reaction of atomic carbon with deuterium oxide (290 mmol) and formaldehyde (0.3-0.5 g) was also expected to increase the yields of higher order carbohydrates relative to glycoaldehyde. However, the molecular weights of the compounds produced were expected to be two mass units smaller than those produced from the carbon and deuterium oxide reactions because the protiated formaldehyde was used as exemplified in equation (55).



(55)

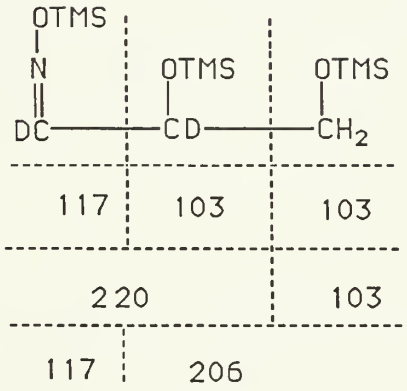
The major fragments expected from Oxime-TMS derivatives of these compounds are shown below:

Glycoaldehyde



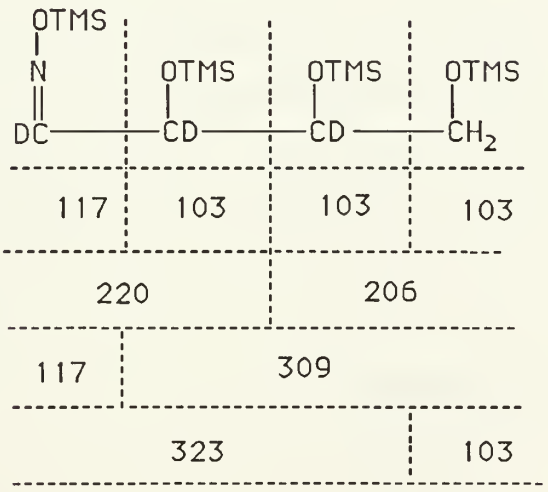
MW= 220

Glyceraldehyde

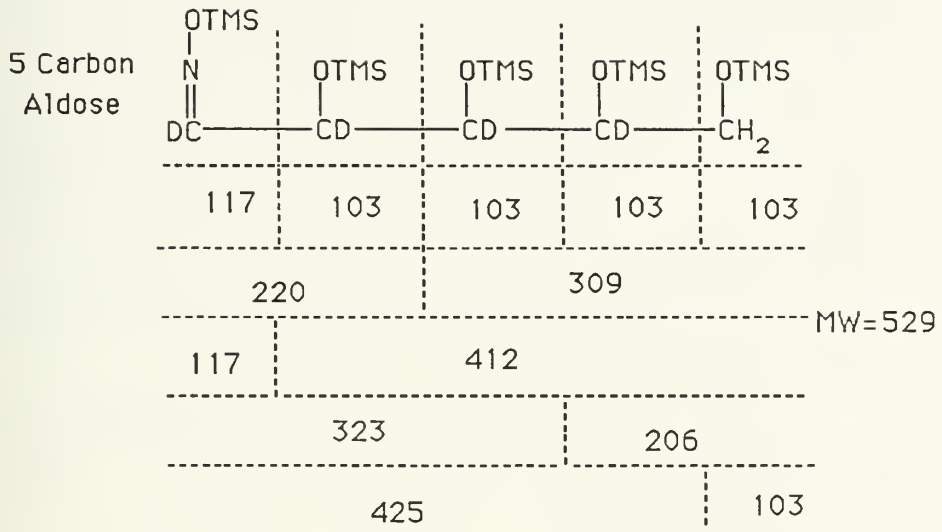


MW= 323

4 Carbon Aldose



MW= 426



Glycoaldehyde (0.0270 ± 0.0036 mmol), glyceraldehyde (0.0110 ± 0.0110 mmol), erythrose (0.0067 ± 0.0049 mmol), and threose (0.0039 ± 0.0040 mmol) were observed. The relative yields of higher order carbohydrates did increase with respect to glycoaldehyde giving results close to those from reaction of carbon with water and formaldehyde. The results were glycoaldehyde (1.0000), glyceraldehyde (0.3861 ± 0.3565), erythrose (0.1784 ± 0.2339), and threose (0.1349 ± 0.1314). Observed Mass Spectral Data from a typical run follow:

Glycoaldehyde

Peak	Retention Time(Sec)
1	670-688
2	689-701

Peak 1: *m/e* 73, 100%; *m/e* 103, 10.86%; *m/e* 105, 5.15%; *m/e* 117, 3.02%; *m/e* 147, 62.67%; *m/e* 205, 1.62%; *m/e* 207, 1.57%; *m/e* 219, 4.53%; *m/e* 220, 1.96%; m/e 221, 1.85%; m/e 222. 0.78%.
Peak 2: *m/e* 73, 100%; m/e 103, 28.65%; *m/e* 105, 7.15%; *m/e* 116, 4.61%; *m/e* 117, 3.32%; *m/e* 119, 2.80%; *m/e* 147, 72,44%; *m/e* 204, 3,37%; *m/e* 205, 4.04%; *m/e* 206, 1.09%; *m/e* 207, 0.78%; *m/e* 220, 0.67%; *m/e* 221, 1.24%; *m/e* 222, 0.73%.

Glyceraldehyde

Peak	Retention Time(Sec)
1	1092-1107
2	1142-1175

Peak 1: *m/e* 73, 100%; *m/e* 103, 55.74%; *m/e* 105, 17.26%; *m/e* 117, 3.90%; *m/e* 118, 1.46%; m/e 119, 1.46%; *m/e* 147, 19.75%; *m/e* 202, 1.03%; *m/e* 205, 0.60%; *m/e* 219, 0.49%; *m/e* 220, 0.81%; *m/e* 321, 0.60%; *m/e* 322, 1.41%; *m/e* 324, 0.65%; *m/e* 325, 0.70;%; *m/e* 326, 0.43%; *m/e* 327, 0.43%. Peak 2: *m/e* 73, 100%; *m/e* 103, 43.74%; *m/e* 105, 20.84%; *m/e* 117, 3.21%; *m/e* 118, 2.20%; *m/e* 119, 1.73%; *m/e* 147, 16.16%; *m/e* 205, 0.58%; *m/e* 206, 0.83%; m/e 207, 0.50%; *m/e* 208, 1.12%; *m/e* 218, 0.69%; *m/e* 220, 1.26%; *m/e* 221, 3.43%; *m/e* 306, 0.54%; *m/e* 307, 0.50%; *m/e* 308, 0.61%; m/e 309, 0.32%; *m/e* 310, 1.26%; *m/e* 321, 0.61%; *m/e* 322, 0.50%; *m/e* 323, 0.58%; *m/e* 324, 0.72%; *m/e* 325, 1.05%.

Erythrose

Peak	Retention Time(Sec)
1	1428-1444
2	1446-1456
3	1478-1480

Peak 1: *m/e* 73, 100%; *m/e* 103, 86.12%; *m/e* 105, 35.19%; *m/e* 116, 6.69%; *m/e* 117, 9.42%; *m/e* 118, 4.69%; *m/e* 119, 1.86%; *m/e* 120, 2.73%; *m/e* 147, 32.71%; *m/e* 202, 2.85%; *m/e* 205, 1.12%; *m/e* 221, 0.99%; *m/e* 320, 1.98%; *m/e* 321, 1.49%; *m/e* 322 1.12%; *m/e* 411, 0.74%; *m/e* 423, 1.61%; *m/e* 424, 1.49%; *m/e* 426, 0.99%.

Peak 2: *m/e* 73, 100%; *m/e* 103, 59.23%; *m/e* 105, 9.58%; *m/e* 116, 2.45%; *m/e* 117, 2.10%; *m/e* 118, 1.87%; *m/e* 119, 1.64%; *m/e* 120, 1.87%; *m/e* 147, 35.63%; *m/e* 204, 2.22%; *m/e* 206, 0.82%; *m/e* 208, 0.93%; *m/e* 216, 2.92%; *m/e* 320, 9.81%; *m/e* 321, 3.86%; *m/e* 322, 1.99%; *m/e* 323, 1.64%; *m/e* 424, 0.70%.

Peak 3: *m/e* 73, 86.55%; *m/e* 103, 41. 82%; *m/e* 105, 10.55%; *m/e* 117, 32.36%; *m/e* 118. 21.82%; *m/e* 119, 8.73%; *m/e* 120, 8.00%; *m/e* 147, 100%; *m/e* 205, 7.27%; *m/e* 206, 5.09%; *m/e* 208, 3.27%; *m/e* 219, 5.45%; *m/e* 220, 4.73%; *m/e* 221, 2.91%; *m/e* 321, 4.00%; *m/e* 428, 2.18%.

Threose

Peak	Retention Time(Sec)
1	1458-1469
2	1491-1498

Peak 1: *m/e* 73, 100%; *m/e* 103, 68.01%; *m/e* 105, 36.95%; *m/e* 117, 12.82%; *m/e* 118, 8.10%; *m/e* 147, 39.80%;*m/e* 205, 1.69%; *m/e* 206, 2.04%; *m/e* 207, 0.87, *m/e* 208, 1.63%; *m/e* 221, 1.34%; *m/e* 320, 4.78%; *m/e* 322, 2.68%; *m/e* 323, 3.03%; *m/e* 324, 1.22%; *m/e* 423, 1.63%; *m/e* 424, 1.22%; *m/e* 425, 0.82%; *m/e* 428, 0.58%.

Peak 2: *m/e* 73, 86.73%; *m/e* 103, 17.99%; *m/e* 105, 16.22%; *m/e* 116, 3.69%; *m/e* 117, 9.88%; *m/e* 118, 9.88%; *m/e* 119, 6.93%; *m/e* 120, 27.88%; *m/e* 147, 100%; *m/e* 205, 1.77%; *m/e* 207, 1.62%; *m/e* 208, 10.18%; *m/e* 219, 1.77%; *m/e* 220, 2.80%; *m/e* 221, 4.28%; *m/e* 222, 2.06%; *m/e* 321, 1.77%; *m/e* 322, 2.80%; *m/e* 323, 1.77%; *m/e* 324, 1.33%; *m/e* 413, 1.03%.

Pentoses

Peak	Retention Time(Sec)
1	1722-1734
2	1735-1741
3	1742-1753

Peak 1: *m/e* 73, 100%; *m/e* 103, 73.53%; *m/e* 105, 14.55%; *m/e* 116, 10.09%; *m/e* 117, 34.34%; *m/e* 118, 18.48%; *m/e* 119, 9.44%; *m/e* 147, 54.18%; *m/e* 202, 2.62%; *m/e* 205, 2.88%; *m/e* 206, 2.36%; *m/e* 217, 1.05%; *m/e* 218, 0.79%; *m/e* 221, 1.18%; *m/e* 525, 7.47%; *m/e* 526, 15.60%; *m/e* 527, 19.40%; *m/e* 528, 9.57%; *m/e* 529, 2.88%; *m/e* 530, 4.46%; *m/e* 531, 1.44%.

Peak 2: *m/e* 73, 71.91%; *m/e* 103, 44.82%; *m/e* 105, 22.41%; *m/e* 116, 3.34%; *m/e* 117, 13.38%; *m/e* 118, 16.05%; *m/e* 120, 18.39%; *m/e* 147, 100%; *m/e* 205, 3.34%; *m/e* 206, 4.01%; *m/e* 207, 3.34%; *m/e* 208, 7.69%; *m/e* 217, 1.67%; *m/e* 321, 5.35%; *m/e* 322, 13.71%; *m/e* 323,

4.68%; *m/e* 324, 5.69%; *m/e* 325, 5.35%; *m/e* 423, 4.35%; *m/e* 424, 2.01%; *m/e* 453, 3.01%.

Peak 3: *m/e* 73, 74.38%; *m/e* 103, 33.06%; *m/e* 105, 21.76%; *m/e* 116, 6.06%; *m/e* 117, 12.95%; *m/e* 118, 15.43%; *m/e* 119, 7.16%; *m/e* 120, 16.80%; *m/e* 147, 100%; *m/e* 205, 4.96%; *m/e* 206, 4.96%; *m/e* 207, 2.48%; *m/e* 208, 3.58%; *m/e* 321, 7.44%; *m/e* 322, 8.26%; *m/e* 323, 4.96%; *m/e* 324, 4.13%; *m/e* 325, 4.41%; *m/e* 423, 2.48%; *m/e* 512, 1.93%; *m/e* 525, 2.48%; *m/e* 527, 1.93%.

For statistical completeness all of the reactions of carbon with H_2O and D_2O were grouped together, and their mean values and standard deviations were calculated and tabulated in Tables 3 and 5. This appears reasonable since the carbohydrate yield was apparently independent of the amounts of water utilized, and because H_20 and D_20 are chemically equivalent. The resulting figures for relative yields were glycoaldehyde (1.0000), glyceraldehyde (0.2533 ± 0.1163), erythrose (0.0987 ± 0.0676) and threose (0.1142 ± 0.0973). A similar grouping was performed for reactions of carbon vapor with formaldehyde which gave glycoaldehyde (1.0000), glyceraldehyde (0.2450 ± 0.2300), erythrose (0.1608 ± 0.1366) and threose (0.2953 ± 0.3408). These groupings are identified in Tables 3 and 5 by the H_2O/D_2O marking.

Table 6 is a compiliation of the relative intensities of the *m/e* 's from the mass spectral data of the various reactions. This data conclusively supports the mechanism of addition of hydroxymethylene to aldehydes, involving a five-center six-electron transition state similar to that pictured in equation (55).

Further supporting evidence was provided by *m/e* 105, CD_2OTMS, which was present in all of the products of the reaction of carbon vapor with D_2O. The protiated counterpart of this fragment ion, CH_2OTMS, has *m/e* 103 and was commom to all of the undeuterated aldoses. The presence of *m/e* 105 in the deuterated compounds indicates that atomic carbon reacts with D_2O to form fully deuterated formaldehyde. The deuterated formaldehyde then reacts with another deuterated hydroxymethylene to form glycoaldehyde. The dominance of *m/e* 103 over *m/e* 105 in the products arising from the reaction of protiated formaldehyde with carbon vapor and D_2O further confirms the proposed mechanism because the two protons present in the CH_2OTMS species could only come from the protiated formaldehyde as predicted by equation (55).

The parent ion of protiated glycoaldehyde gives *m/e* 219 in the mass spectrum. Fragments *m/e* 220, 221, and 222 most likely arise from ion molecule reactions of *m/e* 219 with protons in the ion trap detector. These fragments shift to *m/e* 220, 222, and 224 in the deuterated reactions indicating full deuterium incorporation. The fragments *m/e* 220 and 224 can be interpreted as M-2 and M+2 corresponding to the loss or gain of a deuterium. Similar results occur for the M-15 fragment, *m/e* 204, which shifts to *m/e* 207 in deuterated reactions. The reactions of formaldehyde with D_2O show a relatively even spread from *m/e* 204 to *m/e* 207 indicating that both partially deuterated and fully deuterated glycoaldehyde was formed.

Similar conclusions can be drawn from the ananlysis of the glyceraldehyde data. The protiated compound possesses a parent ion of *m/e* 321 and a M-15 peak of *m/e* 306. The observed values

were *m/e* 321, 322, and 323 for the parent ion and *m/e* 306, 307 and 308 for the M-15 peak. These peaks shift to *m/e* 325, 326 and 327 for the parent ion and *m/e* 310 and 311 for the M-15 peak in the reactions of carbon vapor with D_2O. In the formaldehyde plus D_2O reactions, the M-15 peak is spread over the range of *m/e* 306 to 310 with the larger intensities occurring around *m/e* 308 and *m/e* 310. The parent ion is centered around *m/e* 324 and 325.

The identification and separation of erythrose and threose is one of the most significant findings of this research. This result indicates that hydroxymethylene does indeed add to higher aldehydes via the five-center six-electron transition state proposed. The parent ion for protiated compounds is *m/e* 423 which was observed in both erythrose and threose. These peaks shift to *m/e* 428 in the deuterated species and are spread over the range of *m/e* 423 to 428 in the formaldehyde plus D_2O reactions. The M-15 peak should shift from *m/e* 408 in the protiated species to *m/e* 413 in deuterated species. For threose the *m/e* 408 was observed in the second peak eluted in the reaction of carbon with H_2O as expected. But no M-15 fragments were observed in the deuterated run. This was propably an effect of low concentration of the sugar in the sample. However, *m/e* 413 was the only M-15 peak observed in the formaldehyde and D_2O reactions. This combined with the fact that *m/e* 103 dominated over *m/e* 105 peak by aprroximately 4 to 1 in threose produced in the formaldehyde and D_2O reactions provides strong support for the proposed mechanism of addition of hydroxymethylene. Simialr results were obtained for erythrose.

Table 6

Relative Intensities in $C+H_2O$, $C+D_2O$, and $C+H_2O+H_2CO$ Reactions.

Product	*m/e*	$C + H_2O$		$C\ D_2O$		$C + D_2O + H_2CO$	
Peak—>		I	II	I	II	I	II
Glycoaldehyde	73	100	100	100	100	100	100
	103	27.2	32.0	6.5	-	8.39	28.65
	104	8.15	12.86	7.31	8.54	6.21	10.73
	105	1.81	3.45	25.7	30.02	5.15	7.15
	116	2.34	2.71	-	1.07	1.51	4.61
	117	3.35	1.38	3.95	3.74	3.02	3.32
	118	1.12	1.43	1.49	1.53	1.68	1.71
	119	1.01	0.74	1.49	1.33	1.62	2.80
	120	-	0.69	0.91	1.07	1.62	1.09
	130	10.28	17.10	0.52	-	6.49	11.45
	147	28.38	22.08	35.34	27.69	62.67	72.44
	204	0.53	23.07	-	-	0.78	3.37
	205	1.60	6.80	-	0.67	1.62	4.04
	206	-	2.12	-	0.73	0.84	1.09
	207	-	0.39	1.49	22.48	1.57	0.78
	208	-	-	0.78	4.00	-	-
	219	0.43	0.54	-	-	4.5	-
	220	2.4	5.13	-	-	1.96	0.67
	221	3.41	1.18	2.20	-	1.85	1.24
	222	0.80	0.44	-	-	0.78	0.73
	223	-	-	1.68	2.07	-	-
	224	-	-	1.88	3.47	-	-
	225	-	-	0.45	-	-	-

Table 6 (Con't)

Relative Intensities in $C+H_2O$, $C+D_2O$, and $C+H_2O+H_2CO$ Reactions

Product	*m/e*	$C + H_2O$		$C\ D_2O$		$C + D_2O + H_2CO$	
Peak—>		I	II	I	II	I	II
Glyceraldehyde	73	100	100	100	100	100	100
	103	30.73	50.55	14.99	8.09	55.74	43.74
	104	3.30	11.41	3.75	3.76	15.80	17.92
	105	1.21	1.90	28.11	43.01	17.26	20.84
	114	0.56	0.49	-	-	0.43	-
	115	-	-	-	-	0.60	0.50
	116	-	0.55	-	0.82	0.76	0.79
	117	5.31	3.19	-	0.82	3.90	3.21
	118	1.05	1.10	-	-	3.41	2.20
	119	-	-	-	-	1.46	1.73
	120	-	-	3.35	1.14	2.11	1.84
	130	-	-	-	-	-	0.50
	131	1.69	0.86	-	1.14	2.44	1.62
	132	-	-	-	-	0.87	1.08
	133	1.93	0.74	1.87	1.55	6.01	3.53
	146	-	-	-	0.65	0.87	1.08
	147	9.73	11.42	9.64	10.55	19.75	16.16
	148	1.29	-	1.87	2.78	5.36	7.32
	204	-	-	-	2.13	-	0.29
	205	0.72	2.39	-	-	0.60	0.58
	206	-	-	-	-	-	0.83
	207	-	0.55	-	-	-	0.50
	208	-	-	-	-	-	1.12
	218	0.88	0.98	-	-	-	0.69
	219	-	-	-	-	0.49	1.19
	220	-	-	1.47	1.96	0.81	1.26

Table 6 (Con't)

Relative Intensities in $C+H_2O$, $C+D_2O$, and $C+H_2O+H_2CO$ Reactions.

Product	*m/e*	$C + H_2O$		$C\ D_2O$		$C + D_2O + H_2CO$	
Peak—>		I	II	I	II	I	II
	221	-	5.77	-	5.07	0.81	3.43
Glyceraldehyde	306	-	6.13	-	-	-	0.54
	307	-	1.47	-	-	-	0.50
	308	-	0.55	-	-	-	0.61
	309	-	-	-	-	-	0.32
	310	-	-	-	6.05	-	1.26
	311	-	-	-	1.31	-	-
	321	5.47	2.21	-	-	0.60	0.61
	322	2.49	0.86	-	-	1.41	0.50
	323	0.80	-	-	-	-	0.58
	324	-	-	-	-	0.65	0.72
	325	-	-	8.84	2.04	0.70	1.05
	326	-	-	3.48	0.78	0.43	-
	327	-	-	-	0.98	0.43	-
Threose	73	100	100	100	100	100	100
	103	63.50	15.04	8.20	6.08	68.01	17.99
	104	6.26	2.21	6.97	-	45.69	8.11
	105	3.07	-	73.77	21.55	36.95	16.22
	114	5.18	-	-	-	5.19	-
	115	3.67	-	-	-	5.77	2.36
	116	4.10	-	9.43	-	4.95	3.65
	117	11.45	19.03	-	-	12.82	9.88
	118	2.16	-	-	-	8.10	9.88
	119	-	-	3.69	-	5.01	6.93
	120	-	-	6.15	16.02	5.42	27.88
	128	2.81	-	-	-	2.89	1.18
	129	2.38	1.99	-	-	2.89	1.18

Table 6 (Con't)

Relative Intensities in $C+H_2O$, $C+D_2O$, and $C+H_2O+H_2CO$ Reactions

Product	*m/e*	$C + H_2O$		$C\ D_2O$		$C + D_2O + H_2CO$	
Peak—>		I	II	I	II	I	II
Threose	130	1.30	-	-	-	2.56	1.62
	131	2.16	1.99	3.28	-	4.08	3.39
	132	-	-	-	-	4.08	2.95
	147	18.14	32.08	24.18	39.78	39.80	100
	148	-	-	-	7.18	16.78	29.06
	204	-	-	-	-	0.87	-
	205	2.38	-	-	-	1.69	1.77
	206	-	--	-	-	2.04	-
	207	-	-	-	-	0.87	1.62
	208	-	-	-	-	1.63	10.18
	217	-	1.33	-	-	-	-
	218	-	-	-	-	0.76	0.88
	219	-	2.65	-	-	-	1.77
	220	-	-	-	-	1.11	2.80
	221	-	-	-	-	1.34	4.28
	222	-	-	-	4.42	0.76	2.06
	320	16.85	1.99	-	-	4.78	-
	321	4.32	-	-	-	3.55	1.77
	322	5.40	-	-	-	2.68	2.80
	323	-	-	25.41	10.50	3.03	1.77
	324	-	-	5.74	-	1.22	1.33
	408	-	2.21	-	-	-	-
	413	-	-	-	-	-	1.03
	423	6.26	1.33	-	-	1.63	-
	424	-	-	-	-	1.22	-
	425	-	-	-	-	0.82	-
	428	-	-	9.84	7.18	0.58	-

Table 6 (Con't)

Relative Intensities in $C+H_2O$, $C+D_2O$, and $C+H_2O+H_2CO$ Reactions

		$C + H_2O$			$C + D_2O$			$C + D_2O + H_2CO$		
Erythrose	*m/e*	I	II	III	I	II	III	I	II	III
	73	100	100	100	100	100	100	100	100	100
	103	77.9	40.6	23.5	7.04	-	13.64	86.1	59.2	41.8
	104	5.42	3.83	3.09	11.6	12.3	-	26.2	15.1	10.9
	105	2.21	-	-	78.9	34.2	19.7	35.2	9.58	10.6
	114	3.41	-	-	-	-	-	4.34	2.57	2.18
	115	3.21	-	-	-	-	-	2.73	1.75	3.64
	116	4.82	-	2.89	4.23	-	-	6.69	2.45	-
	117	6.63	34.5	30.9	-	-	-	9.42	2.10	32.4
	118	2.21	4.15	5.98	-	-	-	4.96	1.87	21.9
	119	-	-	-	3.17	-	-	1.86	1.64	8.73
	120	-	-	-	-	27.4	25.8	2.73	1.87	8.00
	128	3.61	-	-	-	-	-	3.22	-	-
	129	2.41	3.19	1.65	-	-	-	2.60	3.27	-
	130	-	-	3.09	-	-	-	2.60	3.27	-
	131	-	-	2.06	-	-	-	3.84	4.79	6.91
	132	-	-	-	-	-	-	2.23	2.22	-
	133	3.21	3.51	1.44	3.52	-	-	6.44	6.89	7.64
	147	17.1	53.7	42.9	14.4	-	50.7	32.7	35.6	100
	204	-	-	-	2.82	-	-	-	2.22	-
	205	-	-	-	-	-	-	1.12	-	7.27
	206	-	-	-	-	-	-	--	0.82	5.09
	208	-	-	-	-	-	6.08	-	0.93	3.27
	216	-	-	-	-	-	-	-	2.92	-
	217	-	-	-	-	-	-	-	4.09	-
	219	-	-	-	-	-	-	-	1.29	5.45
	220	-	-	-	-	-	-	-	-	4.73

Table 6 (Con't)

Relative Intensities in $C+H_2O$, $C+D_2O$, and $C+H_2O+H_2CO$ Reactions

		$C + H_2O$			$C + D_2O$			$C + D_2O + H_2CO$		
Erythrose	*m/e*	I	II	III	I	II	III	I	II	III
	221	-	-	-	-	-	-	0.99	-	2.91
	320	-	-	-	-	-	-	1.98	9.81	-
	321	-	-	-	-	-	-	1.49	3.86	4.00
	322	-	-	-	-	-	-	1.12	1.99	-
	323	-	-	-	15.1	20.6	7.58	-	1.64	-
	324	-	-	-	3.52	-	-	-	-	-
	411	-	-	-	-	-	-	0.74	-	-
	423	7.43	-	-	-	-	-	1.61	-	-
	424	2.61	-	-	-	-	-	1.49	0.70	-
	426	-	-	-	-	-	-	0.99	-	-
	428	-	-	-	14.4	-	-	-	-	2.18
	429	-	-	-	4.58	-	-	-	-	-

The pentose sugars arabinose, lyxose, ribose, and xylose were especially difficult to separate and identify because of overlapping peaks. Usually six peaks were eluted beginning with the first peak of lyxose, and followed by the first peak of xylose. Next came a combined peak of lyxose and xylose that partially overlapped the first peak of arabinose. Then the second peak of arabinose and lastly the two peaks of ribose which occasionally overlapped. The elution order of these sugars is displayed in Table 1. The protiated Oxime–TMS derivatives of these sugars were identified by the presence of *m/e* 's 103, 320, 510, and 525 in their mass spectra and deuterated pentoses were expected to be identified by observation of *m/e* 's 105, 325, 516, and 531 in their mass spectra. That these sugars were also products of the reaction of atomic carbon with water was most clearly demonstrated by data obtained from the reactions of

carbon vapor with D_2O listed on pages 65 and 66. The retention times for peaks 2 through 7 listed there correspond directly to the retention times of the known standards. However, the first peak was eluted earlier than any of the Oxime—TMS standards of these compounds (1718-1726 sec). The peaks were not much larger than baseline noise and therefore no quantitization data is reported here. The pentoses were also present in the reactions of carbon vapor with water and in those employing D_2O and formaldehyde. The presence of these sugars as reaction products provides additional evidence for the mechanism of addition of hydroxymethylene involving a five—center six—electron transition state. In an effort to determine the minimum amount of the pentoses detectable by the ion trap detector a standard solution containing 0.01 mg (6.7×10^{-5} mmol) of each sugar was prepared, converted to a trimethylsilylated oxime, and analyzed. The resulting chromatogram contained small peaks with the appropriate retention time. However, only *m/e* 's 73, 103, and 147 were present in their mass spectra. Therefore 6.7×10^{-5} mmol was accepted as indicating a trace amount. The apparently simple reaction of atomic carbon with water produces some very complicated results. There were a multitude of peaks in the chromatogram of the reaction products. In this research attention was focused upon the aldoses, but there were obviously more products than these. In an effort to identify some of the peaks and ensure that the Oxime-TMS derivatization process was complete simple TMS derivatives were prepared to check their retention times and mass sprctra on the DB-5 capillary column. In addition several simple alcohols, erythritol, threitol, and ribitol were

converted to TMS derivatives and analyzed. For completeness, this additional data is provided in the expereimental section of the thesis. Also, the known presence of dihydroxyacetone in these reactions provides for the potential presence of ketoses occuring among the products. Next in this series are the four carbon ketose, erythrulose, and five carbon ketoses, ribulose and xylulose.

Further research in this area could provide additional understanding of the mechanisms of reaction of hydroxymethylene. Because hydroxymethylene is a potential interstellar species this information could be applied to understanding the methods of carbohydrate formation in interstellar space, particularly in comets and on the Jovian planets.

III. CONCLUSIONS

The experimental work has shown that in addition to glycoaldehyde and glyceraldehyde, it is possible to produce erythrose, threose and to a small degree the pentoses arabinose, lyxose, ribose and xylose by the reaction of water vapor with carbon vapor generated in a high intensity arc.

The carbohydrates produced are apparently formed via the reaction of hydroxymethylene with formaldehyde and subsequently produced higher order aldoses. These reactions occur via a five-center six-electron transition state. Supporting evidence for this theory was provided by complete deuterium incorporation into the products when the reactions were performed in the presence of water vapor generated from deuterium oxide. Futher evidence for the proposed mechanism was provided by a noticeable increase in the yield of all aldoses with respect to glycoaldehyde when formaldehyde was distilled into the reactor as one of the reactants. In addition, when deuterium oxide was reacted with formaldehyde and carbon vapor partial deuterium incorporation in the products occured with exception of the two protons arising from the protiated formaldehyde.

The Finnigan-MAT Ion Trap Detector provides a fast, reliable, and convenient means of performing gas chromatography/mass spectroscopy analysis. The mass spectral data obtained were comparable with that of conventional mass spectrophotometers.

IV. EXPERIMENTAL

Physical Measurements

Nuclear Magnetic Reasonance (NMR) analysis were performed on Varian EM-390 90 MHz and Bruker AM-400 400 MHz NMR spectrometers. Gas chromatographic/Mass Spectral data were obtained via Varian 3700 Gas Chromatograph interfaced to either a Finnigan MAT-700 Ion Trap Data System or Vacuum Generators (VG) Analytical 7000E Mass Spectrophotometer.

The following gas chromatographic columns were utilized:

Column A: Altech Chirasil-Val III, 25 m x 0.25 mm.

Column B: J and W,fused silica capillary,DB-5-30N,30 m x 0.252 mm.

Gas Chromatography Temperature Program: 50 °C for 1 min, 5 °C per minute heatup rate to 280 °C. Infrared spectroscopic measurements were performed on Perkin Elmer 580 and 983 spectrophotometers.

Materials

The following chemicals were purchased from various sources and used without further purification: Glycoaldehyde, glyceraldehyde, erythrose, ribose, lyxose, arabinose, xylose, glucose, galactose, mannose, erythritol, threitol, ribitol, hydroxylamine, hydrochloride, pyridine, trimethylchlorosilane, trifluoroacetic acid, 1,1,1,3,3,3-hexamethyldisilazane, 1,3-dihydroxyacetone, paraldehyde, sulfuric acid, sodium meta periodate, nitrogen, high purity carbon electrodes, sodium bicarbonate, sodium hydroxide, ammonium hydroxide, methanol, ethanol, ethyl acetate,

barium carbonate, and acetic acid. All other chemicals used were either available in the Chemistry Supply Store or synthesized.

Preparation of Standard Sugars and Sugar Alcohols

Individual standard solutions of glycoaldehyde, glyceraldehyde, erythrose, threose, arabinose, lyxose, ribose, xylose, mannose, galactose, glucose, erithritol, threitol, and ribitol were prepared by dissolving 100 mg in 100 ml of distilled water.

Preparation of Oxime Derivatives of Standard Sugars[105]

Various combinatons of the standard sugars were converted to oxime derivatives by dissolving 200 mg hydroxylamine hydrochloride in a known volume of the sugar or sugar alcohol. The solution was frozen, placed under vacuum, allowed to thaw and heated at 80°C in an oil bath while being magnetically stirred for one to one and one half hours. Dried oxime derivatives were then obtained by placing the solution under vacuum on a rotary evaporator.

Preparation of Trimethylsilyl Derivatives[101,105]

The species to be silylated, either a sugar, its oxime derivative, or a sugar alcohol, was dissolved in 1.0 ml of pyridine. This solution was then placed under vacuum and hexamethyldisilizane (0.5 ml) and chlorotrimethylsilane (0.25 ml) were added. The soluton was then shaken for one minute and placed under N_2 overpressure. After being allowed to stand for at least fifteen minutes the solutions were analyzed by Gas Chromatography/Mass Spectrometry using the Ion Trap Detector.

Mass Spectral Data and Retention Times Using the DB-5 Capillary Column

All Oxime-TMS derivatives were apparently acyclic as evidenced by the presence of two peaks in the chromatagram indicating the formation of both *syn* and *anti* isomers of the oximes as expected.[104] The first peak eluted usually contained the parent ion (M) as a dominant peak and the second larger peak contained a peak corresponding to the parent ion minus fifteen mass units (M-15) formed by the well known loss of a silicon linked methyl group. This indicates that the major isomer was *syn* with both bulky groups on opposite sides of the carbon nitrogen double bond.

The gas chromatography/mass spectral data for the standars used are provided below. The data presented was collected on a DB-5-30N capillary column using a temperature program of 50°C for 1 minute then a 5°C per minute heatup rate to 280°C. Helium pressure on the gas chromatograph was set at 20 psig. Split injections were made with the splitter off for the first 45 seconds. The Split ratio was 60:1. Retention times are in seconds and are given as a range corresponding to the width of each peak.

Hydroxylamine TMS GC/MS Data:

Peak	Retention Time (sec)
1	350-370

Peak 1 Mass Spectral Data: *m/e* 73,32.16%; *m/e* 103, 2.07%; *m/e* 132, 94.05%; *m/e* 147, 43.24%; *m/e* 162, 100%; *m/e* 177, 33.24%, *m/e* 234, 16.22%; *m/e* 249, 4.86%.

Glycoaldehyde Oxime-TMS GC/MS Data:

Peak	Retention Time (sec)
1	660-690
2	691-710

Peak 1 Mass Spectral Data: *m/e* 73, 61.40%, *m/e* 100, 44.1%, *m/e* 103, 84.46%; *m/e* 130, 42.61%; *m/e* 147, 100%; *m/e* 149, 21.30%; *m/e* 204, 4.76%; *m/e* 220, 14.54%; *m/e* 221, 13.53%.
Peak 2 Mass Spectral Data: *m/e* 73, 62.76%; *m/e* 100, 39.80%; *m/e* 103, 100%; *m/e* 130, 54.08%; *m/e* 147, 68.37%, *m/e* 149, 11.73%; *m/e* 204, 78.83%; *m/e* 219, 2.30%, *m/e* 220, 21.17%, *m/e* 221, 4.59%.

Glyceraldehyde Oxime-TMS GC/MS Data:

Peak	Retention Time(sec)
1	1090-1110
2	1150-1185

Peak 1 Mass Spectral Data: *m/e* 73, 74.84%; *m/e* 100, 100%; *m/e* 103, 65.29%, *m/e* 117, 28.34%, *m/e* 147, 30.25% *m/e* 189, 46.82%; *m/e* 200, 17.52%; *m/e* 205,12.74%; *m/e* 306, 2.23%; *m/e* 321, 11.15%; *m/e* 322, 9.24%; *m/e* 323, 3.50%.
Peak 2 Mass Spectral Data: *m/e* 73, 91.39%; *m/e* 100, 100%, *m/e* 103, 57.68%; *m/e* 117, 25.09%; *m/e* 147, 62.55%; *m/e* 191, 19.48%;*m/e* 205, 48.69%; *m/e* 221, 38.20%; *m/e* 306, 84.27%; *m/e* 321, 10.49%; *m/e* 322, 15.73%

1,3 Dihydroxyacetone Oxime-TMS GC/MS Data:

Peak	Retention Time(sec)
1	1130-1170

Peak 1 Mass Spectral Data: *m/e* 73, 100%; *m/e* 100, 11.25%, *m/e* 103, 89.99% ; m/e 113, 0.62%; *m/e* 114, 1.12%; *m/e* 115. 0.73% ; *m/e* 147, 6.75%; *m/e* 191, 1.63%; *m/e* 192, 1.29%; *m/e* 202, 14.33%; *m/e* 203, 6.24%;
m/e 221, 0.61%; *m/e* 246, 3.09% ; *m/e* 306, 13.21%; *m/e* 321, 2.02%; *m/e* 322,1.63% ; *m/e* 323, 0.62%.

Erythrose Oxime-TMS GC/MS Data:

Peak	Retention Time(sec)
1	1440-1460
2	1475-1500

Peak 1 Mass Spectral Data: *m/e* 73, 24.44%; *m/e* 100, 55.56%; *m/e* 103, 50.00%; *m/e* 117, 68.89%; *m/e* 147, 100%; *m/e* 292, 10.00%; *m/e* 320, 50.00%, *m/e* 423, 7.78%.
Peak 2 Mass Spectral Data: *m/e* 73, 79.41%; *m/e* 100, 50.98%; *m/e* 103, 100%; *m/e* 117, 61.76%; *m/e* 147, 43.14%; *m/e* 172, 14.71%; *m/e* 217, 41.18%; *m/e* 320 7.84%; *m/e* 408, 47.06%, *m/e* 409, 25.49%; *m/e* 410, 8.82%; *m/e* 411, 11.76%.

Threose Oxime-TMS GC/MS Data:

Peak	Retention Time (sec)
1	1455-1470
2	1490-1515

Peak 1 Mass Spectral Data: *m/e* 73, 58.10%; *m/e* 100, 88.57%; *m/e* 103, 100%; *m/e* 117, 85.71%; *m/e* 147, 74.29%; *m/e* 217, 52.38%; *m/e* 291, 25.71%; *m/e* 334, 20.00%; *m/e* 424, 5.71%

Peak 2 Mass Spectral Data: *m/e* 73, 87.25%; *m/e* 100, 37.25%; *m/e* 103, 100%; *m/e* 117, 53.92%; *m/e* 147, 50.00%; *m/e* 217, 50.00%; *m/e* 319, 11.76%; *m/e* 334, 11.76%; *m/e* 408, 77.45%; *m/e* 409, 30.39%; *m/e* 410, 16.67%; *m/e* 424, 5.88%.

Arabinose Oxime-TMS GC/MS Data:

Peak	Retention Time (sec)
1	1760-1770
2	1771-1780

Peak 1 Mass Spectral Data: *m/e* 73, 22.12%; *m/e* 100. 17.31%; *m/e* 103, 100%; *m/e* 117, 25.00%; *m/e* 147, 25.00%; *m/e* 217, 9.62%; *m/e* 256, 14.42%; *m/e* 292 15.38%; *m/e* 307, 31.73%; *m/e* 320, 18.27%; *m/e* 450, 6.73%; *m/e* 510, 8.65%.

Peak 2 Mass Spectral Data: *m/e* 73, 9.09%; *m/e* 100, 21.21%; *m/e* 103, 100%; *m/e* 147, 6.06%; *m/e* 251, 11.62%; *m/e* 256, 11.11%; *m/e* 257, 6.06% *m/e* 278, 11.11%; *m/e* 307, 39.39%; *m/e* 320, 42.93%; *m/e* 450, 5.05%; *m/e* 525, 7.58%.

Lyxose Oxime-TMS GC/ MS Data:

Peak	Retention Time (sec)
1	1735-1745
2	1755-1765

Peak 1 Mass Spectral Data: *m/e* 73,10.00%; *m/e* 100, 29.00%; *m/e* 103, 100%; *m/e* 147, 9.00%; *m/e* 251, 14.00%; *m/e* 291, 10.00%; *m/e* 307, 99.00%; *m/e* 320, 77.00%, *m/e* 450, 9.00%; *m/e* 456, 7.00%; *m/e* 525, 34.00%; *m/e* 526, 9.00%.

Peak 2 Mass Spectral Data: *m/e* 73, 16.30%; *m/e* 100, 19.26%; *m/e* 103, 100%; *m/e* 117, 8.89%; *m/e* 147, 18 52%; *m/e* 217, 11.85%; *m/e* 250, 15.56%; *m/e* 256, 28.89%; *m/e* 278, 23.70%; *m/e* 292%; *m/e* 307, 50.37%; *m/e* 320, 38.52%; *m/e* 250, 8.15%; *m/e* 511, 8.89%; *m/e* 512, 7.41%; *m/e* 525, 11.85%; *m/e* 527, 11.85%; *m/e* 528, 6.67%.

Ribose Oxime-TMS GC/MS Data:

Peak	Retention Time (sec)
1	1780-1790
2	1791-1805

Peak 1 Mass Spectral Data: *m/e* 73, 7.94%; *m/e* 100, 17.69%; *m/e* 103, 100%; *m/e* 117, 4.08%; *m/e* 147, 5.44%; *m/e* 217, 5.90%; *m/e* 252, 4.76%; *m/e* 307, 19.27%; *m/e* 320, 23.58%; *m/e* 454, 1.59%; *m/e* 525, 14.06%; *m/e* 526, 4.08%; *m/e* 527, 2.27%; *m/e* 528, 3.40%.

Peak 2 Mass Spectral Data: *m/e* 73, 14.91%; *m/e* 100, 10.03%; *m/e* 103, 100%; *m/e* 117, 10.30%; *m/e* 147, 13.01%; *m/e* 217, 4.61%; *m/e* 307, 7.86%; *m/e* 320, 6.78%; *m/e* 510, 2.71%; *m/e* 511, 1.90%; *m/e* 525, 2.44%.

Xylose Oxime-TMS GC/MS Data:

Peak	Retention Time (sec)
1	1745-1755
2	1756-1770

Peak 1 Mass Spectral Data: *m/e* 73, 6.43%; *m/e* 100, 19.64%; *m/e* 103, 100%; *m/e* 117, 3.04%; *m/e* 147, 5.36%; *m/e* 217, 6.25%; *m/e* 307, 6.43%; *m/e* 308, 15.18%; *m/e* 320, 20.71%; *m/e* 454, 1.79%; *m/e* 525, 6.43%; *m/e* 526, 1.96%.

Peak 2 Mass Spectral Data: *m/e* 73, 13.18%; *m/e* 100, 12.92%; *m/e* 103, 100%; *m/e* 117, 9.04%; *m/e* 147, 11.89%; *m/e* 217, 4.65%; *m/e* 307, 10.34%; *m/e* 320, 10.34%; *m/e* 510, 8.53%; *m/e* 511, 3.62%; *m/e* 525, 4.13%; *m/e* 527, 1.29%.

Glucose Oxime-TMS GC/MS Data:

Peak	Retention Time (sec)
1	2035-2075
2	2076-2100

Peak 1 Mass Spectral Data: *m/e* 73, 71.50%; *m/e* 100, 30.05%; *m/e* 103, 100%; *m/e* 117, 19.69%; *m/e* 129, 32.12%; *m/e* 147, 19.17%; *m/e* 157, 18.13%; *m/e* 191, 21.24%; *m/e* 218, 35.75%; *m/e* 250, 12.95%; *m/e* 254, 10.36%; *m/e* 268, 10.36%; *m/e* 320, 27.98%; *m/e* 433, 13.47%; *m/e* 522, 5.18%; *m/e* 613, 6.22%.

Peak 2 Mass Spectral Data: *m/e* 73, 34.98%; *m/e* 100, 43.11%; *m/e* 103, 100%; *m/e* 117, 13.43%; *m/e* 129, 24.73%; *m/e* 147, 34.63%; *m/e* 157, 24.03%; *m/e* 205, 11.66%; *m/e* 217, 10.95%; *m/e* 319, 81.27%; *m/e* 405, 2.47%; *m/e* 432, 3.18%.

Galactose Oxime-TMS Data:

Peak	Retention Time (sec)
1	2025-2055
2	2056-2095

Peak 1 Mass Spectral Data: *m/e* 73, 63.89%; *m/e* 100, 27.78%; *m/e* 103, 100%; *m/e* 117, 9.26%; *m/e* 129, 23.61%; *m/e* 147, 25.93%; *m/e* 157, 15.74%; *m/e* 191, 11.57%; *m/e* 217, 42.13%; *m/e* 252, 10.65%;

Peak 2 Mass Spectral Data: *m/e* 3.87%; *m/e* 100, 34.82%; *m/e* 103, 100%; *m/e* 117, 14.70%; *m/e* 129, 23.96%; *m/e* 147, 32.59%; *m/e* 157, 20.45%; *m/e* 217, 16.61%; *m/e* 319, 67.73%; *m/e* 402, 3.19%; *m/e* 448, 2.88%

Mannose Oxime-TMS GC/MS Data:

Peak	Retention Time (sec)
1	2045-2075
2	2080-2110

Peak 1 Mass Spectral Data: *m/e* 73, 18.60%; *m/e* 103, 91.86%; *m/e* 117, 19.77%; *m/e* 129, 27.91%; *m/e* 147, 39.53%; *m/e* 157, 15.12%; *m/e* 205, 12.79%; *m/e* 217, 13.95%; *m/e* 268, 10.47%; *m/e* 306, 12.79%; *m/e* 307, 11.63%; *m/e* 319, 100%; *m/e* 320, 40.70%; *m/e* 345, 9.30%; *m/e* 613, 8.14%.

Peak 2 Mass Spectral Data: *m/e* 73, 9.50%; *m/e* 100, 25.14%; *m/e* 103, 58.10%; *m/e* 117, 9.50%; *m/e* 129, 18.99%; *m/e* 147, 25.70%; *m/e* 157, 16.76%; *m/e* 206. 8.38%; *m/e* 251, 4.47%; *m/e* 268, 5.59%; *m/e* 291, 4.47%; *m/e* 319, 22.91%; *m/e* 320, 100%; *m/e* 332, 7.26%; *m/e* 523, 3.91%; *m/e* 538, 5.03%.

Glycoaldehyde TMS GC/MS Data:

Peak	Retention Time (sec)
1	1015-1055

Peak 1 Mass Spectral Data: *m/e* 73, 12.15%; *m/e* 101, 40.67%; *m/e* 102, 19.41%, *m/e* 103, 14.74%; *m/e* 116, 20.44%; *m/e* 117, 100%; *m/e* 118, 40.15%; *m/e* 119, 19.85%; *m/e* 120, 6.74%; *m/e* 205, 7.26%; *m/e* 263, 6.37%.

Glyceraldehyde TMS GC/MS Data:

Peak	Retention Time (sec)
1	1720-1760
2	1765-1780
3	1781-1795

Peak 1 Mass Spectral Data: *m/e* 73, 70.20%; *m/e* 103, 81.18%; *m/e* 116, 45.10%; *m/e* 117, 24.31%; *m/e* 129, 28.24%; *m/e* 147, 20.00%; *m/e* 189, 15.69%; *m/e* 199, 39.22%; *m/e* 219, 85.49%; *m/e* 250, 6.67%; *m/e* 273, 9.02%; *m/e* 291, 23.52%; *m/e* 307, 45.88%; *m/e* 452, 2.75%; *m/e* 468, 4.71%.

Peak 2 Mass Spectral Data: *m/e* 73, 8.64%; *m/e* 103, 100%; *m/e* 117, 5.40%; *m/e* 129, 12.96%; *m/e* 147, 8.86%; *m/e* 173, 13.61%; *m/e* 189, 7.13%; *m/e* 217, 2.38%; *m/e* 233, 1.94%; *m/e* 263, 48.38%; *m/e* 273, 1.51%; *m/e* 291, 3.46%; *m/e* 307, 3.89%; *m/e* 319, 1.94

Peak 3 Mass Spectral Data: *m/e* 73, 9.45%; *m/e* 103, 100%; *m/e* 117, 4.65%; *m/e* 129, 7.95%; *m/e* 147, 7.80%; *m/e* 173, 13.64%; *m/e* 189, 5.85%; *m/e* 217, 4.50%; *m/e* 263 47.83%; *m/e* 291, 3.45%; *m/e* 307, 3.45%.

1,3-Dihydroxyacetone TMS GC/MS Data:

Peak	Retention Time (sec)
1	1720-1755
2	1770-1805

Peak 1 Mass Spectral Data: *m/e* 73, 42.99%; *m/e* 103, 100%; *m/e* 117, 2.14%; *m/e* 130, 13.78%; *m/e* 147, 4.51%; *m/e* 189, 6.65%; *m/e* 199, 9,03%; *m/e* 219, 70.07%; *m/e* 260, 2.38%; *m/e* 275, 11.88%; *m/e* 291, 13.06%; *m/e* 307, 31.83%; *m/e* 317, 3.56%.

Peak 2 Mass Spectral Data: *m/e* 73, 47.20%; *m/e* 103, 100%; *m/e* 129, 33.04%; *m/e* 147, 9.73%; *m/e* 171, 2.65%; *m/e* 189, 9.44%; *m/e* 199, 12.68%; *m/e* 243, 9.44%; *m/e* 275, 21.53%; *m/e* 291, 10.62%; *m/e* 307, 5.31%; *m/e* 317, 5.60%; *m/e* 365, 14.16%; *m/e* 366, 5.90%.

Arabinose TMS GC/MS Data:

Peak	Retention Time (sec)
1	1540-1585
2	1595-1605
3	1625-1635

Peak 1 Mass Spectral Data: *m/e* 73, 100%; *m/e* 103, 21.47%; *m/e* 129, 12.57%; *m/e* 147, 9.42%; *m/e* 169, 8.90%; *m/e* 191, 41.36%; *m/e* 217, 61.78%; *m/e* 243, 10.47%; *m/e* 259, 91.62%; *m/e* 291, 8.90%; *m/e* 305, 16.23%; *m/e* 307, 7.85%; *m/e* 333, 37.70%; *m/e* 393, 3.66%; *m/e* 450, 3.66%.

Peak 2 Mass Spectral Data: *m/e* 73, 80.68%; *m/e* 103, 56.82%; *m/e* 117, 12.50%; *m/e* 129, 20.45%; *m/e* 147, 37.50%; *m/e* 191, 90.91%;

m/e 204, 34.09%; *m/e* 217, 100%; *m/e* 243, 9.09%; *m/e* 259, 29.55%; *m/e* 279, 13.64%; *m/e* 305, 32.95%; *m/e* 333, 12.50%.

Peak 3 Mass Spectral Data: *m/e* 73, 41.48%; *m/e* 103, 57.39%; *m/e* 129, 14.20%; *m/e* 147, 21.59%; *m/e* 189, 3.98%; *m/e* 217, 100%; *m/e* 259, 9.09%; *m/e* 291, 6.82%; *m/e* 305, 15.91%; *m/e* 307, 5.11%; *m/e* 333, 15.34%; *m/e* 335, 3.41%.

Lyxose TMS GC/MS Data:

Peak	Retention Time (sec)
1	1530-1565
2	1590-1630

Peak 1 Mass Spectral Data: *m/e* 73, 100%; *m/e* 103, 42.21%; *m/e* 117, 12.99%; *m/e* 129, 34.42%; *m/e* 147, 14.29%; *m/e* 169, 14.94%; *m/e* 191, 32.47%; *m/e* 204, 54.55%; *m/e* 217, 49.35%; *m/e* 243, 14.94%; *m/e* 259, 63.64%; *m/e* 279, 11.69%; *m/e* 305, 18.18%; *m/e* 307, 7.14%; *m/e* 333, 22.73%; *m/e* 393, 5.19%; *m/e* 450, 5.84%; *m/e* 452, 5.19%.

Peak 2 Mass Spectral Data: *m/e* 73, 100%; *m/e* 103, 44.62%; *m/e* 116, 132.85%; *m/e* 129, 18.46%; *m/e* 147, 8.72%; *m/e* 169, 13.33%; *m/e* 189, 12.31%; *m/e* 191, 41.03%; *m/e* 204, 30.77%; *m/e* 217, 23.59%; *m/e* 243, 15.90%; *m/e* 259; 64.10%; *m/e* 333, 27.18%; *m/e* 393, 3.08%; *m/e* 437, 3.59%; *m/e* 450, 4.10%.

Ribose TMS GC/MS Data:

Peak	Retention Time (sec)
1	1570-1650

Peak 1 Mass Spectral Data: *m/e* 73, 100%, *m/e* 103, 50.51%; *m/e* 117, 6.12%; *m/e* 129, 15.82%; *m/e* 147, 13.27%; *m/e* 191, 22.96%; *m/e* 204, 10.71%; *m/e* 217, 50.00%; *m/e* 243, 14.80%; *m/e* 259, 37.24%; *m/e* 291, 7.14%; *m/e* 305, 16.84%; *m/e* 333, 34.69%; *m/e* 437, 4.59%; *m/e* 450, 3.57%.

Xylose TMS GC/MS Data:

Peak	Retention Time (sec)
1	1665-1710

Peak 1 Mass Spectral Data: *m/e* 73, 100%; *m/e* 103, 36.17%; *m/e* 116, 6.38%; *m/e* 129; 36.17%; *m/e* 147, 10.11%; *m/e* 191, 30.85%; *m/e* 204, 34.04%; *m/e* 217, 22.87%; *m/e* 259, 94.68%; *m/e* 265, 29.79%; *m/e* 305, 13.83%; *m/e* 333, 31.38%; *m/e* 393, 7.45%.

Erythritol TMS GC/MS Data:

Peak	Retention Time (sec)
1	1320-1355
2	1370-1415

Peak 1 Mass Spectral Data: *m/e* 73, 25.09%; *m/e* 103, 100%; *m/e* 117, 34.15%; *m/e* 147, 12.89%; *m/e* 189, 5.57%; *m/e* 205, 5.23%; *m/e* 221, 4.88%; *m/e* 249, 2.78Z%; *m/e* 321, 2.09%.

Peak 2 Mass Spectral Data: *m/e* 73, 34.80%; *m/e* 103,100%; *m/e* 117, 38.77%; *m/e* 129, 21.59%; *m/e* 147, 19.82%; *m/e* 189, 16.30%; *m/e* 205, 21.59%; *m/e* 217, 17.18%; *m/e* 231, 4.85%; *m/e* 305, 5.73%; *m/e* 321, 9.69%; *m/e* 322, 3.52%.

Threitol TMS GC/MS Data:

Peak	Retention Time (sec)
1	1375-1410

Peak 1 Mass Spectral Data: *m/e* 73, 35.46%; *m/e* 103, 100%; *m/e* 117, 35.86%; *m/e* 129, 13.94%; *m/e* 147, 17.93%; *m/e* 189, 18.73%; *m/e* 205, 16.33%; *m/e* 217, 13.15%; *m/e* 305, 7.57%; *m/e* 321, 35.06%; *m/e* 322, 8.76%; *m/e* 395, 2.79%.

Ribitol TMS GC/MS Data:

Peak	Retention Time (sec)
1	1710-1735

Peak 1 Mass Spectral Data: *m/e* 73, 27.27%; *m/e* 103, 100; *m/e* 117, 12.63%; *m/e* 129, 50.00%; *m/e* 147, 13.13%; *m/e* 189, 13.13%; *m/e* 203, 7.58%; *m/e* 217,16.67%; *m/e* 243, 24.24%; *m/e* 317, 14.14%; *m/e* 319, 18.18%; *m/e* 331, 3.03%.

Preparation of 4,6-O-Ethylidene-D-Galactose[103]

To a suspension of D-galactose (100 mesh, 50 g) in paraldehyde (200 ml) was added concentrated sulfuric acid (0.5 ml) and the mixture was mechanically stirred for twenty-four hours. Ammonium hydroxide (1.5 ml) was then added and the mixture was filtered. The residue was washed with cold ethanol and air dried, then dissolved in hot ethanol, filtered to remove D-galactose and allowed to recrystalize. Yield, 11.12 g, after two recrystallizations from ethanol. Melting point, 180-185°C. The structure was confirmed by IR, 90 MHz ^{1}H NMR, 400 MHz ^{1}H NMR, and 100 MHz ^{13}C NMR.

IR Data: 3500, 3344, 2935, 2883, 2326, 1782, 1691, 1651, 1446, 1408, 1377, 1339, 1272, 1224, 1161, 1136, 1100, 1078, 1052, 1022, 981, 962, 931, 871, 860, 846, 803, 757, 722, 224.

NMR Data: 4,6—O—Ethylidene—D—Galactose

^{13}C at 100 MHz	Chemical Shift (ppm)	Intensity
	100.4081	4.276
	97.4144	3.310
	94.0412	3.007
	76.9739	3.013
	76.5557	3.007
	72.6704	4.567
	69.8495	3.561
	69.6518	2.963
	69.3877	3.272
	68.8289	3.218
	67.7280	3.878
	63.6777	2.705
	21.0587	5.027

^{1}H at 400 MHz	Chemical Shift (ppm)	Intensity
	5.2697	2.252
	4.8660	3.692
	4.8551	3.489
	4.7993	8.162
	4.6094	2.079
	4.5898	2.021
	4.1518	2.949
	4.0963	2.970
	4.0635	1.264
	3.9995	9.057
	3.9686	4.711
	3.9186	4.711
	3.8374	1.670
	3.8115	1.141
	3.7145	1.053
	3.6907	1.436
	3.6269	3.501
	3.5502	0.852
	3.5276	1.158
	3.5058	0.468
	1.3179	12.910

Preparation of 2,4-O-Ethylidene-D-Threose[103]

A solution of 4,6-O-ethylidene-D-galactose (5.15 g, 0.025 mol) in 25 ml water was added during a one hour period to a stirred solution of sodium metaperiodate (11.5 g, 0.055 mol) in water (87.5 ml). The solution was kept at 25 °C by externally cooling and at pH 6 by periodic addition of 2*N* sodium hydroxide. After an additional three hours at room temperature, the solution was adjusted to pH 7.5 and lypholized. The residue was extracted three times with 75 ml portions of hot ethyl acetate and the extracts were concentrated and cooled. The crystalline product was collected and dried. Yield, 1.5 g, melting point, 163-168 °C after recrystallization from ethanol. The structure was confirmed by 90 MHz ^{1}H NMR, IR, 400 MHz NMR ^{1}H and 100MHZ ^{13}C NMR.

IR Data: 3335, 2980, 2940, 2884, 2328, 1691, 1458, 1405, 1379, 1326, 1300, 1249, 1164, 1108, 1091, 1074, 1063, 991, 947, 923, 911, 890, 849, 831, 810, 770, 723, 675, 639 cm^{-1}.

400 MHz NMR Data: 2,4—O—Ethylidene—D—Threose

^{13}C at 100MHZ	Chemical Shift (ppm)	Intensity
	100.5445	4.030
	100.1408	1.933
	99.9886	2.564
	97.1558	1.360
	94.5122	1.386
	92.5217	2.510
	91.8842	2.037
	89.4031	1.099
	81.7606	1.136
	79.6694	2.390
	79.5363	1.423
	72.8372	3.361
	72.5754	1.609
	72.3200	3.324
	70.6436	1.955
	70.0646	2.169
	69.7343	1.927
	67.7856	18.752
	63.6173	1.085
	63.0582	4.180
	20.9805	6.471

^{1}H at 400MHZ	Chemical Shift (ppm)	Intensity
	5.3727	0.753
	5.3565	0.765
	5.1928	1.178
	5.1273	1.128
	4.9430	2.733
	4.9337	2.788
	4.8066	20.532
	4.1084	1.010
	4.0868	1.254
	4.0246	5.605
	3.9865	4.340
	3.9432	1.355
	3.9277	1.234
	3.8697	3.426
	3.8077	1.829
	3.7525	44.115
	3.6412	0.804
	1.3483	13.384

Preparation of Threose[106]

Crystalline 2,4-O-ethylidene-D-threose (0.5140 g) in 0.25*N* sulfuric acid (50 ml) was hydrolyzed at the boiling temperature for thirty minutes, with nitrogen bubbled through the solution resulting in a quantitative distillation of acetaldehyde. The hydrolyzate was neutralized by portionwise addition of barium carbonate. The resulting solution was filtered through celite and deionized by batch addition of Dowex–50X (H^+) resin. The resin was filtered and washed. The combined filtrate and washing was concentated under vacuum to a light yellow clear syrup. Yield, 0.42 g. The structure was confirmed by IR, 90 MHz ^1H NMR, 400 MHz ^1H NMR, and 100 MHZ ^{13}C NMR , and Gas Chromatography/ Mass Spectral Analysis of the Oxime-TMS derivative.

IR Data: 3377, 2926, 2326, 1651, 1402, 1305, 1036, 722, 223, 199,
188 cm-1.

NMR Data: D-Threose

^{13}C at	Chemical Shift (ppm)	Intensity
100 MHz	103.2474	6.086
	97.7118	3.706
	90.9238	1.152
	81.7881	5.570
	78.2980	0.849
	77.3166	3.891
	76.2152	2.575
	75.9904	2.034
	74.3580	1.158
	74.0923	8.128
	71.5997	1.850
	67.7998	35.454
	64.0871	2.239

^1H at 400 MHZ	Chemical Shift (ppm)	Intensity
	5.3830	1.969
	5.2217	4.626
	5.0064	0.699
	4.9924	0.672
	4.9085	0.620
	4.7972	12.062
	4.2819	2.132
	4.1964	4.807
	4.1691	3.406
	4.1562	2.992
	4.1141	0.772
	4.0301	6.377
	3.9457	3.114
	3.9238	2.878
	3.8922	1.287
	3.8642	1.416
	3.8310	1.948
	3.7894	2.025
	3.7271	74.212
	3.6923	2.636
	3.6444	3.636
	3.6210	2.944
	3.5429	0.826
	3.5159	0.618
	3.4473	0.684

Preparation of 4,6-O-Ethylidene-D-Glucose[103]

To a mechanically stirred suspension of Dextrose (50 g) in paraldehyde (200 ml) was added 0.5 ml sulfuric acid. The solution was mechanically stirred for twenty-four hours, then 1.5 ml of ammonium hydroxide was added to neutralize the acid. The residue was filtered and washed with ethanol. The white crystalline solid, 32.0 g , was then recrystallized from ethanol. Yield 20.19 g, melting point, 144-152 °C . The structure was confirmed by IR, 90 MHz ^1H NMR, 400 MHz ^1H NMR, and 100 MHz ^{13}C NMR.

IR Data: 3482, 3319, 3006, 2976, 2951, 2929, 2885, 2326, 1744, 1651, 1392,1374, 1349, 1321, 1295, 1281,1226, 1158, 1102, 1082, 1023, 991, 932, 917, 880, 834, 754, 721, 672, 636, 586, 269, 189 cm^{-1}.

NMR Data: 4,6—O—Ethylidene—D—Glucose

^{13}C at 100 MHZ	Chemical Shift (ppm)	Intensity
	101.0953	6.111
	97.8250	6.649
	94.1365	2.524
	81.2537	3.103
	80.7388	4.947
	76.2551	6.252
	73.7679	4.902
	73.3325	3.267
	71.0368	2.447
	69.0478	3.638
	68.6718	6.876
	67.8076	7.467
	67.1891	6.101
	63.4088	2.627
	20.4834	7.841

^{1}H at 400 MHz	Chemical Shift (ppm)	Intensity
	5.2243	1.262
	5.2153	1.359
	4.8921	1.307
	4.8799	3.420
	4.8671	3.468
	4.8550	1.388
	4.7993	8.883
	4.7005	3.205
	4.1798	1.465
	4.1577	1.843
	4.1467	1.800
	4.0911	0.920
	3.8278	1.106
	3.8049	1.535
	3.7810	1.213
	3.7342	25.027
	3.6540	2.730
	3.6330	5.026
	3.6095	2.895
	3.5976	1.780
	3.5872	1.220
	3.4630	1.743
	3.4410	4.346
	3.4212	3.203
	3.3936	0.982
	3.2988	1.590
	3.2775	2.486
	3.2566	1.288

Preparation of 2,4-O-Ethylidene-D-Erythrose[102]

A solution of 4,6-O-ethylydene-D-glucose (10.3 g, 0.05 mol) in 50 ml water was added during a one hour period to a stirred solution of sodium meta periodate (23.0 g, 0.11 mol) in water (175 ml). The solution was kept at 25 °C by externally cooling in an ice bath and at pH 6 by periodic addition of 2*N* sodium hydroxide. After an additional three hours at room temperature, the solution was adjusted to pH 7.5 and lypholized. The residue was extracted three times with 75 ml portions of hot ethyl acetate and the extracts were concentrated and cooled. The crystalline product was collected and dried. Yield, 6.8727 g. The structure was confirmed by IR, 90 MHz ^{1}H NMR, 400 MHz ^{1}H NMR and 100 MHz ^{13}C NMR.

IR Data: 3398, 2928, 2856, 2326, 1736, 1651, 1458, 1402, 1377, 1291, 1230, 1160, 1081, 1053, 893, 842, 803, 722,671 cm^{-1}.

NMR Data: 2,4—O—Ethylidene—D—Erythrose

^{13}C at 100 MHz	Chemical Shift (ppm)	Intensity
	100.6298	0.629
	100.3268	10.718
	89.1800	8.048
	83.0357	5.131
	80.7249	0.640
	76.2520	0.788
	73.7505	0.665
	70.5791	5.202
	67.7996	6.790
	62.4526	10.187
	20.5977	8.876

^1H at 400 MHz	Chemical Shift (ppm)	Intensity
	18.0945	0.851
	5.2120	4.205
	4.8529	1.778
	4.8409	3.928
	4.8282	4.144
	4.8028	12.499
	4.1481	2.592
	4.1348	2.873
	4.1214	2.907
	4.1081	2.742
	3.7507	16.250
	3.7305	2.549
	3.7189	1.962
	3.7055	1.558
	3.6706	1.023
	3.6514	1.688
	3.6345	1.406
	3.5224	4.698
	3.4937	5.324
	3.4667	2.472

Preparation of Erythrose[106]

Crystalline 2,4-O-ethylidene- D-erythrose (0.7060 g) in 0.25*N* sulfuric acid (70 ml) was hydrolyzed at the boiling temperature for thirty minutes with nitrogen bubbled through the solution resulting in a quantitative distillation of acetaldehyde. The hydrolyzate was neutralized by portionwise addition of barium carbonate. The resulting solution was filtered through celite and deionized by batch addition of Dowex–50X (H^+) resin. The resin was filtered and washed. The combined filtrate and washing was concentated under vacuum to a clear syrup. Yield, 0.58 g. The structure was confirmed by IR, 90 MHz ^1H NMR, 400 MHz ^1H NMR, 100 MHz ^{13}C NMR, and Gas Chromatography/ Mass Spectral Analysis of the Oxime-TMS derivative.

IR Data: 3385, 2936, 2465, 1724, 1554, 1412, 1046, 223, 200 cm^{-1}.

NMR Data: Erythrose

^{13}C at 100 MHz	Chemical Shift (ppm)	Intensity
	102.2607	5.373
	97.1029	1.751
	96.6444	1.644
	90.5451	1.672
	77.4666	12.101
	77.0460	1.336
	76.9774	1.457
	75.3390	1.325
	74.9261	1.212
	74.6983	1.162
	73.9775	1.225
	72.8034	5.092
	72.6558	1.162
	72.3093	9.918
	71.8525	1.031
	71.5542	11.240
	70.8428	1.512
	70.4535	4.498
	67.8011	16.506
	67.0420	1.562
	64.0842	1.813
	63.6622	2.120
	62.2221	1.124
	61.8212	1.157

^{1}H at 400 MHz	Chemical Shift (ppm)	Intensity
	5.2592	2.834
	5.2482	3.145
	5.2340	6.138
	5.2266	6.766
	5.2017	0.774
	5.1927	0.771
	5.0801	1.502
	5.0703	1.586
	4.9749	0.856
	4.9688	0.909
	4.8549	1.487
	4.8349	2.394
	4.8002	48.033
	4.6202	1.282
	4.5992	1.491
	4.5474	1.950
	4.5214	1.834
	4.4318	0.598
	4.4224	1.142
	4.4129	0.723

^{1}H at 400 MHz	Chemical Shift(ppm)	Intensity
	4.3844	2.192
	4.3737	5.927
	4.3629	6.300
	4.3533	2.851
	4.2621	2.547
	4.2224	0.607
	4.1981	6.186
	4.1859	5.668
	4.1736	6.978
	4.1613	6.164
	4.1292	0.908
	4.1048	2.452
	4.0927	3.940
	4.0802	2.328
	4.0208	2.518
	4.0087	6.479
	3.9990	9.497
	3.9892	5.859
	3.9607	0.824
	3.9446	0.879
	3.9177	4.134
	3.8972	2.916
	3.8906	3.148
	3.8780	2.946
	3.8432	3.321
	3.8329	4.108
	3.8242	3.893
	3.8050	3.684
	3.7893	9.469
	3.7802	10.758
	3.7654	10.241
	3.7553	10.322
	3.7505	8.346
	3.7304	72.560
	3.6941	4.588
	3.6772	3.883
	3.6665	4.148
	3.6543	4.570
	3.6358	3.949
	3.6237	3.444
	3.6078	2.733
	3.5811	1.210
	3.5646	0.987
	3.5448	1.371
	3.5359	1.710
	3.5275	1.892
	3.5180	1.833
	3.5138	1.726

^1H at 400 MHz	Chemical Shift (ppm)	Intensity
	3.5092	1.632
	3.4897	0.812
	3.4786	1.039
	3.4542	1.592
	3.4312	1.940
	3.4120	1.392
	3.3982	0.757
	3.3865	1.557
	3.3745	0.915
	3.3637	1.108
	3.2954	0.620
	3.3398	0.640
	3.2084	1.048
	3.1871	0.574

The Carbon Arc Apparatus

The carbon arc apparatus is a uniquely designed vessel consisting of five major parts: the reactor head, the reactor bottom, cold finger trap, a diffusion pump, and a vacuum pump (Figure 1). The reactor head, reactor bottom and cold finger trap were made of glass. The reactor head contains four attachment ports. Three ports were threaded and were used for insertion of two brass electrode holders and a substrate inlet tube. These ports were sealed by o-rings. The fourth port has been used for attachment of a mercury manometer and was sealed by a needle valve. Each brass electrode holder had a hole for insertion of a graphite electrode which was held in place by a brass screw. The brass elecrode holders were water cooled to dissipate heat thereby allowing for attaining maximum vacuum (Figure 2).

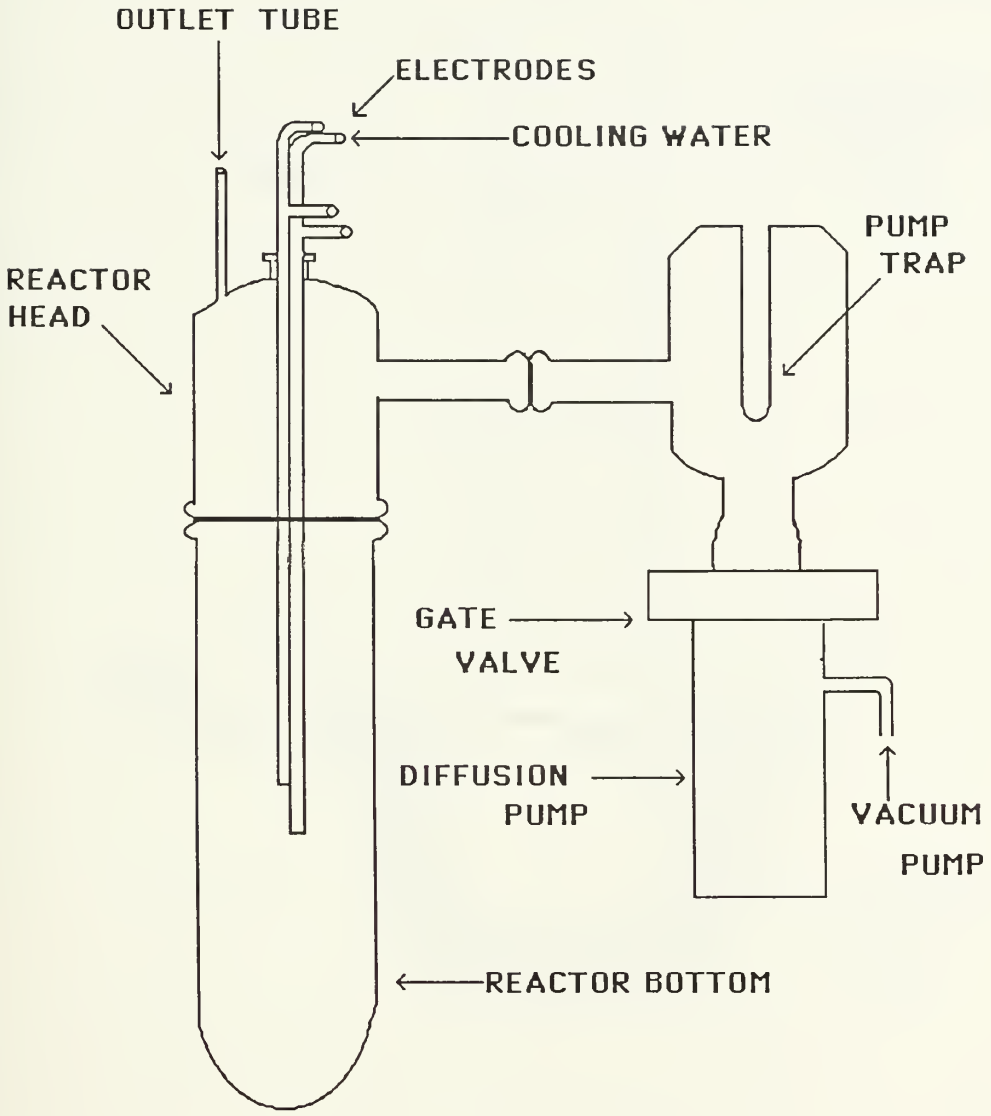


Figure 1: Side View of the Carbon Arc Apparatus

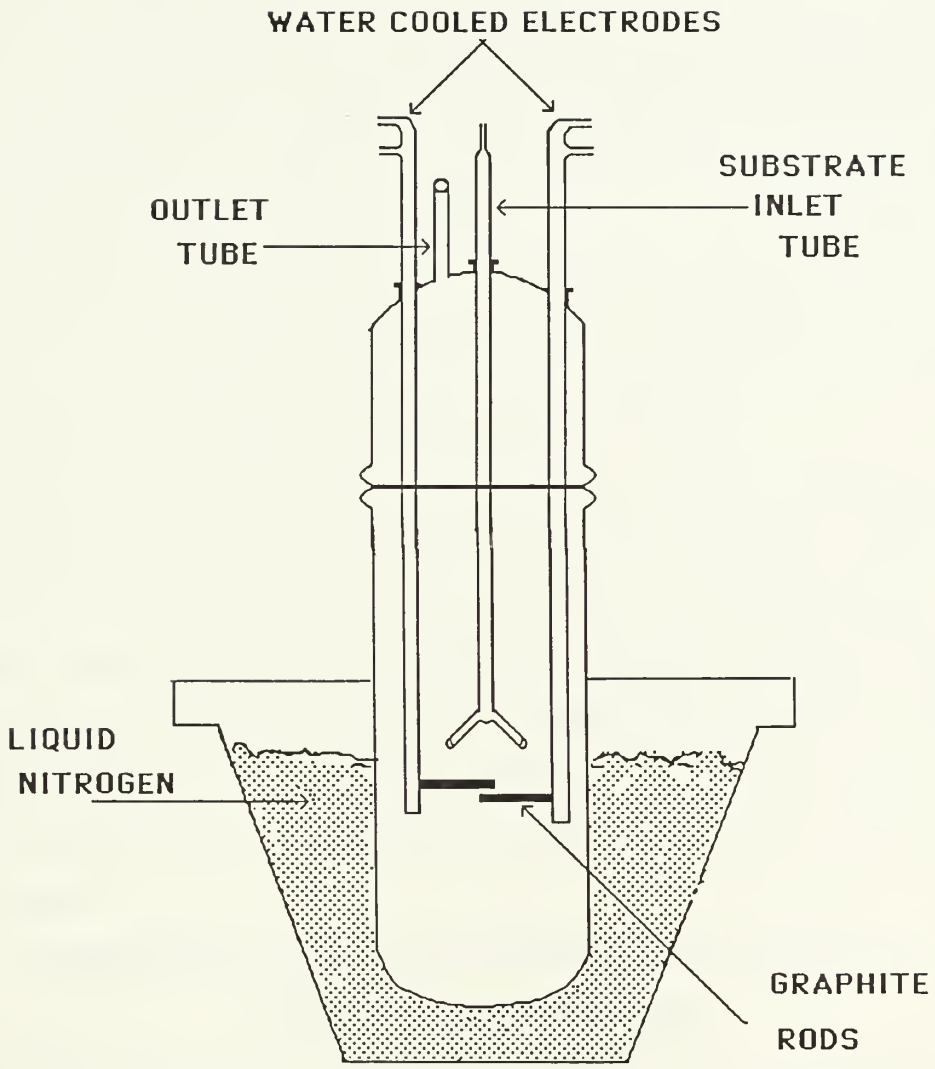


Figure 2: The Carbon Arc Reactor

The joint between the reactor head and reactor bottom was sealed by an o-ring and the two pieces were clamped together by a metal bar held in place by three wing nuts. The joint between the reactor head and cold finger trap was also sealed by an o-ring however,the two pieces were held together by a large vacuum clamp. The cold finger trap rests on an o-ring sealed union secured by a metal bar and three allen head screws atop a 2-inch air operated gate valve. The gate valve served as the boundary between the cold finger trap and the diffusion pump and vacuum pump.

The brass electrode holders were electrically connected to a Sears Craftsman Dual Range 295 Amp arc welder via cables attached by brass connector fittings. The arc welder was set at 70 amps. As a final note, the brass electrode holders and substrate inlet tube were each fitted with a piece of rubber tubing held in place by a hose clamp to prevent them from being inadvertently drawn into the reactor by the high vacuum generated by the diffusion and vacuum pumps.

General Procedure for the Reaction of Arc Generated Carbon Atoms With Substrate

The graphite electrodes were sized and weighed on an analytical balance. They were then inserted into the brass electrode holders tightly secured and the remainder of the carbon arc apparatus was assembled. Once assembly was complete, the vacuum pump was started, the gate valve opened and all unions were checked for leakage. The diffusion pump was started only after pressures were below 5×10^{-2} torr and usually allowed to run for an hour before starting the reaction. Generally, a vacuum of 10^{-5} torr was attained. Liquid nitrogen was used to fill the cold finger trap

and to cool the exterior of the reactor bottom. The arc welder was energized and atomic carbon was then generated by establishing periodic contact between the two graphite electrodes. The atomic carbon produced was condensed on the interior reactor bottom walls at -196 °C along with the substrate(s) which were volatilized into the reactor via a vacuum line or specially designed inlet tube (Figure 3). The rate of substrate entry was controlled by a needle valve. Upon completion of the reaction, the gate valve was shut and diffusion pump was secured. Cooling water was normally allowed to flow through the electode holders and diffusion pump for one hour then it was secured along with the vacuum pump. The liquid nitrogen was removed from the reactor bottom and the vessel was allowed to warm up for approximately twenty-four hours. The carbon arc apparatus was then disassembled, the graphite electrodes were weighed , and nonvolatile products on the interior of the reactor bottom were scraped off and dissolved in distilled water. The resulting solution was then filtered to remove graphite particles and the derivatization process was commenced.

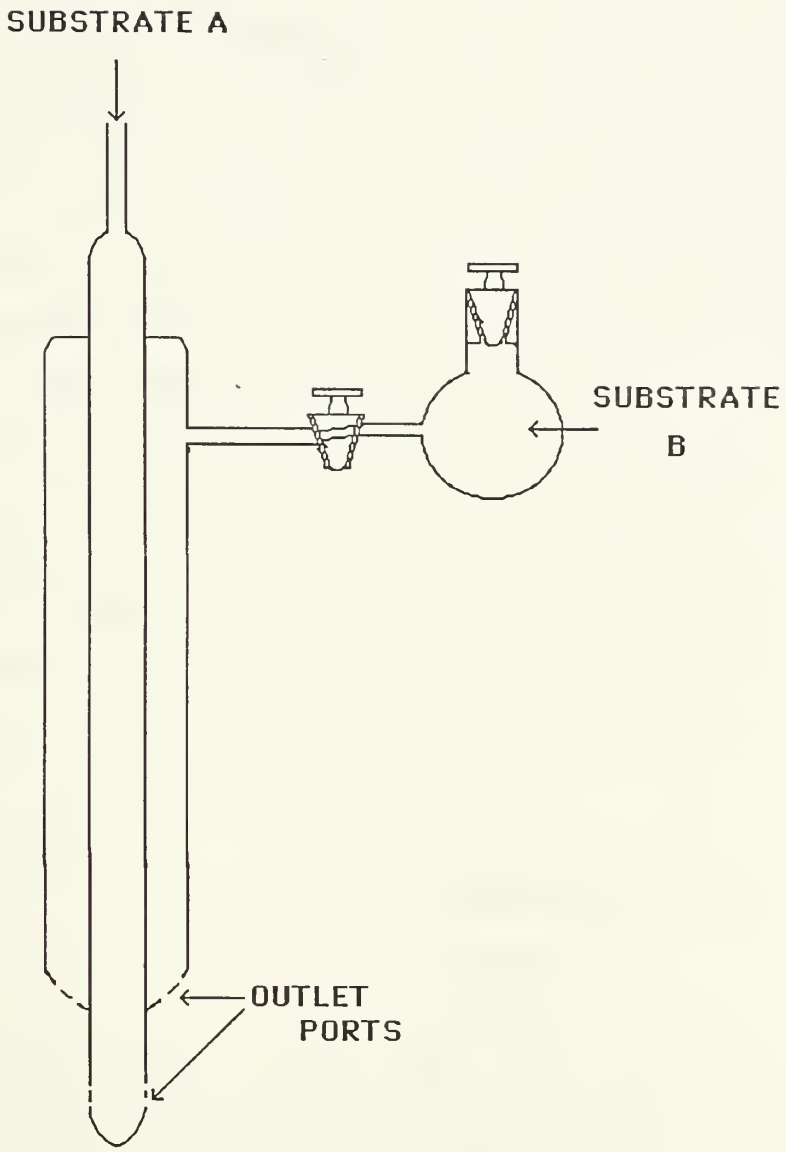


Figure 3: Inlet Tube Utilized for Two Substrates

Reaction of Arc Generated Carbon with Water

Distilled water was volatilized into the carbon arc reactor via a vacuum line and cocondensed on the interior walls of the liquid nitrogen cooled reactor bottom at -196°C with carbon atoms generated by the intermittent striking of an electrical arc between the ends of graphite electrodes. Reactions were performed using either (1.0 mol) or (280 mmol) of water in an effort to determine the effects of water concentration on the yield of products. Upon completion of the reaction, the carbon arc reactor was allowed to warm up for a period of 12 to 24 hours. The reactor was then disassembled and the nonvolatile products which had condensed on the interior wall of the reactor bottom were collected by rinsing with 250-300 ml of distilled water. This solution was then filtered and converted to an Oxime-TMS derivative. The gas chromatography/mass spectral data from a typical run are listed below:

Glycoaldehyde

Peak	Retention Time(Sec)
1	653-680
2	685-702

Peak 1: *m/e* 73, 100%; *m/e* 100, 15.23%; *m/e* 103, 27.21%; *m/e* 115, 1.28%; *m/e* 116, 2.34%; *m/e* 117, 3.35%; *m/e* 130, 10.28%; *m/e* 147, 28.38%; *m/e* 177, 3.46%; *m/e* 204, 0.53%; *m/e* 205, 1.60%; *m/e* 219, 0.43%; *m/e* 220, 2.45%; *m/e* 221, 3.41%; *m/e* 222, 0.80%.

Peak 2: *m/e* 73, 100%; *m/e* 100, 15.92%; *m/e* 103,31.99%; *m/e* 116, 2.71%; *m/e* 117, 1.38%; *m/e* 118, 1.43%; *m/e* 130, 17.10%; *m/e* 147, 22.08%; *m/e* 204, 23.07%; *m/e* 205, 6.80%; *m/e* 218, 0.74%; *m/e* 219, 0.54%; *m/e* 220, 5.13%; *m/e* 221, 1.18%; *m/e* 222, 0.44%.

Glyceraldehyde

Peak	Retention Time(Sec)
1	1083-1097
2	1135-1164

Peak 1: *m/e* 73, 100%; *m/e* 100, 45.62%; *m/e* 103, 30.73%; *m/e* 114, 0.56%; *m/e* 117, 5.31%; *m/e* 118, 1.05%; *m/e* 131, 1.69%; *m/e* 147, 9.73%; *m/e* 189, 6.36%; *m/e* 191, 4.02%; *m/e* 205, 0.72%; *m/e* 218, 0.88%; *m/e* 321, 5.47%; *m/e* 322, 2.49%; *m/e* 323, 0.80%.

Peak 2: *m/e* 73, 100%; *m/e* 100, 38.22%; *m/e* 103; 24.60%; *m/e* 116, 1.04%; *m/e* 117, 5.98%; *m/e* 118,1.67%; *m/e* 147, 14.51%; *m/e* 189, 1.04%; *m/e* 191, 3.75%; *m/e* 295, 5.28%; *m/e* 218, 1.18%; *m/e* 221, 5.91%; *m/e* 232, 1.67%; *m/e* 306, 8.13%; *m/e* 321, 3.27%; *m/e* 322, 2.08%.

Erythrose

Peak	Retention Time(Sec)
1	1421-1435
2	1437-1447
3	1470-1480

Peak 1: *m/e* 73, 100%; *m/e* 100, 10.64%; *m/e* 103, 77.91%; *m/e* 114, 3.41%; *m/e* 115, 3.21%; *m/e* 116, 4.82%; *m/e* 117, 6.63%; *m/e* 118, 2.21%; *m/e* 129, 2.41%; *m/e* 147, 17.07%; *m/e* 172, 4.82%; *m/e* 189, 2.41%; *m/e* 191, 4.82%; *m/e* 231, 3.41%; *m/e* 259, 1.81%; *m/e* 320, 8.23%; *m/e* 336; 1.20%; *m/e* 423, 7.43%; *m/e* 424, 2.61%.

Peak 2: *m/e* 73, 100%; *m/e* 100, 34.50%; *m/e* 103, 40.58%; *m/e* 117, 34.50%; *m/e* 118, 4.15%; *m/e* 129, 3.19%; *m/e* 147, 53.67%; *m/e* 205, 7.67%; *m/e* 217, 4.15%; *m/e* 219, 8.95%; *m/e* 320, 7.03%; *m/e* 321, 4.15%.

Peak 3: *m/e* 73, 100%; *m/e* 100, 12.96%; *m/e* 103, 63.50%; *m/e* 116, 4.10%; *m/e* 117, 11.45%; *m/e* 128, 2.81%; *m/e* 130, 1.30%; *m/e* 147, 18.14%; *m/e* 172, 2.16%; *m/e* 189, 1.73%; *m/e* 205, 2.38%; *m/e* 257, 1.08%; *m/e* 288, 3.46%; *m/e* 320, 16.85%; *m/e* 333, 5.40%; *m/e* 423, 6.26%.

Threose

Peak	Retention Time(Sec)
1	1446-1458
2	1482-1495

Peak 1: *m/e* 73, 100%; *m/e* 100, 12.96%; *m/e* 103, 63.50%; *m/e* 116, 4.10%; *m/e* 117, 11.45%; *m/e* 128, 2.81%; *m/e* 130 1.30%; *m/e* 147, 18.14%; *m/e* 172, 2.16%; *m/e* 189, 1.73%; *m/e* 202, 2.16%; *m/e* 205, 2.38%; *m/e* 257, 1.08%; *m/e* 288, 3.46%; *m/e* 291, 1.30%; *m/e* 320, 16.85%; *m/e* 333, 5.40%; *m/e* 336, 1.30%; *m/e* 423, 6.26%.

Peak 2: *m/e* 73, 100%; *m/e* 100, 20.58%; *m/e* 103, 15.04%; *m/e* 117, 19.03%; *m/e* 129, 1.99%; *m/e* 131, 1.99%; *m/e* 147, 32.08%; *m/e* 217, 1.33%; *m/e* 219, 2.65%; *m/e* 257, 1.77%; *m/e* 258, 3.54%; *m/e* 261, 1.11%; *m/e* 320, 1.99%; *m/e* 408, 2.21%; *m/e* 423, 1.33%.

Pentoses

Peak	Retention Time(Sec)
1	1730-1740
2	1746-1754
3	1755-1763

Peak 1: *m/e* 73, 100%; *m/e* 100, 14.29%; *m/e* 103, 28.10%; *m/e* 116, 11.90%; *m/e* 117, 22.38%; *m/e* 129, 4.76%; *m/e* 147, 28.10%; *m/e* 191, 2.86%; *m/e* 217, 3.33%; *m/e* 224, 2.38%; *m/e* 257, 6.67%; *m/e* 270, 4.76%; *m/e* 305, 7.14%; *m/e* 321, 16.19%; *m/e* 347, 9.52%; *m/e* 510, 6.19%; *m/e* 525, 3.81%.

Peak 2: *m/e* 73, 47.69%; *m/e* 100, 18.34%; *m/e* 103, 100%; *m/e* 116, 1.44%; *m/e* 117, 6.54%; *m/e* 129, 3.35%; *m/e* 133, 1.59%; *m/e* 147, 10.05%; *m/e* 189, 2.07%; *m/e* 191, 1.44%; *m/e* 217, 10.37%; *m/e* 218, 1.91%; *m/e* 250, 2.23%; *m/e* 254, 144%; *m/e* 277, 4.47%; *m/e* 306, 2.23%; *m/e* 307, 15.47%; *m/e* 320, 7.18%; *m/e* 321, 2.87%; *m/e* 331, 1.12%; *m/e* 450, 3.35%; *m/e* 486, 0.80%; *m/e* 510, 13.88%; *m/e* 525, 6.38%.

Peak 3: *m/e* 73, 60.62%; *m/e* 103, 100%; *m/e* 117, 10.20%; *m/e* 129, 6.23%; *m/e* 130, 1.70%; *m/e* 147, 14.16%; *m/e* 189, 1.98%; *m/e* 217, 10.76%; *m/e* 258, 2.83%; *m/e* 278, 3.68%; *m/e* 305, 3.68%; *m/e* 306, 2.83%; *m/e* 307, 18.70%; *m/e* 320, 10.20%; *m/e* 451, 3.12%; *m/e* 457, 2.27%; *m/e* 463, 3.12%; *m/e* 525, 3.12%; *m/e* 526, 9.63%.

Reaction of Arc Generated Carbon With Water and Formaldehyde

The conversion of hydroxymethylene to formaldehyde is the initial step in the production of higher carbon monosaccharides and theoretically increasing the concentration of formaldehyed at the start of the reaction should increase the yields of carbohydrates. To test the mechanism proposed for the production of carbohydrates paraformaldehyde was placed in the 50 ml bulb of a specially designed inlet tube (Figure 3) and heated to 120-150°C producing formaldehyde which was volatilized into the carbon arc reactor and cocondensed on the walls of the reactor bottom with water and atomic carbon. Gas chromatography and mass spectral data obtained were the similar to that for reactions of carbon with water.

Reaction of Arc Generated Carbon with D_2O

Also in an attempt to clarify the mechanism of reaction of hydroxymethylene, deuterium oxide (250 mmol) was reacted with atomic carbon. Deuterium incorporation into the carbohydrates should give Oxime—TMS derivatives of correspondingly higher molecular weights however, the retention times on the gas chromatograph should be the same.

Oxime -TMS Derivative	Protiated Molecular Weight	Deuterated Molecular Weight
Glycoaldehyde	219	222
Glyceraldehyde	321	325
Erythrose	423	428
Threose	423	428
Arabinose	525	531
Lyxose	525	531
Ribose	525	531
Xylose	525	531

Observed Mass Spectral Data:

Glycoaldehyde

Peak	Retention Time(Sec)
1	668-692
2	693-710

Peak 1: *m/e* 73, 100%; *m/e* 101, 10.16%; *m/e* 103,6.54%; *m/e* 105, 25.76%; *m/e* 117, 3.95%; *m/e* 118, 1.49%; *m/e* 119, 1.49%; *m/e* 132, 1.68%; *m/e* 133, 15.15%; *m/e* 147, 34.34%; *m/e* 207, 1.49%; m/e 208, 0.78%; *m/e* 221, 2.20%; *m/e* 223, 1.68%; *m/e* 224, 1.88%; *m/e* 325, 0.45%.

Peak 2: *m/e* 73, 100%; *m/e* 101, 12.54%; *m/e* 105, 30.02%; *m/e* 116, 1.07%; *m/e* 117, 3.74%; *m/e* 118, 1.53%, *m/e* 119, 1.33%; *m/e* 120, 1.07%; *m/e* 133, 21.95%; *m/e* 147, 27.69%; *m/e* 207, 22.48%; *m/e* 208, 4.00%; *m/e* 209, 1.07%; *m/e* 223, 2.07%; *m/e* 224, 3.47%.

Glyceraldehyde

Peak	Retention Time(Sec)
1	1088-1103
2	1140-1168

Peak 1: *m/e* 73, 100%; *m/e* 101, 49.53%; *m/e* 103, 14.99%; *m/e* 105, 28.11%; *m/e* 120, 3.35%; *m/e* 133, 1.87%; *m/e* 147, 9.64%; *m/e* 192, 4.28%; *m/e* 202, 1.34%; *m/e* 220,1.47%; *m/e* 325, 8.84%; *m/e* 326,3.48.

Peak 2: *m/e* 73, 100%; *m/e* 101, 42.82%; *m/e* 105, 22.92%; *m/e* 119, 0.61%; *m/e* 120, 3.81%; *m/e* 132, 1.38%; *m/e* 133, 1.04%; *m/e* 147, 16.87%; *m/e* 164, 2.16%; *m/e* 192, 3.72%; *m/e* 202, 0.69%; *m/e* 208, 3.25%; *m/e* 220, 1.56%; *m/e* 221, 5.19%; *m/e* 222, 1.38%; *m/e* 310, 3.20%; *m/e* 325, 1.47%; *m/e* 326, 1.90%.

Erythrose

Peak	Retention Time(Sec)
1	1427-1440
2	1443-1449
3	1476-1484

Peak 1: *m/e* 73, 100%; *m/e* 105, 78.87%; *m/e* 116, 4.33%; *m/e* 119, 3.77%; *m/e* 133, 3.52%; *m/e* 147, 14.44%; *m/e* 172, 3.17%; *m/e* 192, 2.46%; *m/e* 204, 2.82%; *m/e* 234, 3.17%; *m/e* 323,15.14%; *m/e* 324, 3.52%; *m/e* 428, 14.44%; *m/e* 429, 4,58%.

Peak 2: *m/e* 73, 100%; *m/e* 101, 28.77%; *m/e* 105, 34.25%; *m/e* 120, 27.40%; *m/e* 147, 39.73%; *m/e* 293, 5.48%; *m/e* 323, 20.55%.

Peak 3: *m/e* 73, 100%; *m/e* 101, 27.27%; *m/e* 103, 13.64%; *m/e* 105, 19.70%; *m/e* 120, 25.76%; *m/e* 147, 50.76%; *m/e* 323, 7.5%.

Threose

Peak	Retention Time(Sec)
1	1453-1465
2	1488-1497

Peak 1: *m/e* 73, 100%; *m/e* 101, 6.97%; *m/e* 103, 8.20%; *m/e* 105, 73.77%; *m/e* 116, 9.43%; *m/e* 119, 3.69%; *m/e* 120, 6.15%; *m/e* 133, 4.92%; *m/e* 147, 24.18%; *m/e* 251, 3.69%; *m/e* 323, 25.41%; *m/e* 324, 5.94%; *m/e* 428, 9.84%.

Peak 2: *m/e* 73, 100%; *m/e* 101, 20.99%; *m/e* 103, 6.08%; *m/e* 105, 21.55%; *m/e* 120, 16.02%; *m/e* 147, 39.78%; *m/e* 222, 4.42%; *m/e* 260, 10.50%; *m/e* 323, 10.50%; *m/e* 341, 2.76%; *m/e* 428, 7.18%.

Pentoses

Peak	Retention Time(Sec)
1	1718-1726
2	1730-1735
3	1737-1747
4	1754-1759
5	1761-1762
6	1764-1768
7	1781-1786

Peak 1: *m/e* 73, 100%; *m/e* 105, 30.56%; *m/e* 147, 25.00%; *m/e* 531, 61.11%.

Peak 2: *m/e* 73, 100%; *m/e* 105, 41.18%; m/e 325, 38.24%.

Peak 3: *m/e* 73, 100%; *m/e* 105, 36.96%; *m/e* 120, 26.09%; *m/e* 147, 50.00%; *m/e* 531, 26.09%.

Peak 4: *m/e* 73, 100%; *m/e* 105, 35.79%: *m/e* 147, 25.00%; *m/e* 308, 17.50%.

Peak 5: *m/e* 73, 100%; *m/e* 105, 35.29%; *m/e* 452, 32.35%.

Peak 6: *m/e* 73, 81.25%; *m/e* 75, 100%; *m/e* 103, 68.75%; *m/e* 105, 28.13%; *m/e* 256, 18.75%; *m/e* 331, 15.63%.

Peak 7: *m/e* 73, 73.08%; *m/e* 75, 100%; *m/e* 105, 46.15%; *m/e* 516, 23.08%.

Reaction of Arc Generated Carbon With Formaldehyde and D_2O

To confirm the proposed mechanism and increase the yields of higher order carbohydrates reactions of carbon vapor with formaldehyde and deuterium oxide were performed. Addition of deuterated hydroxymethylene to formaldehyde and subsequently produced monosaccharides should ultimately yield Oxime-TMS derivatives containing two less deuteriums than the reactions with deuterium oxide alone. Molecular weights expected are shown below.

Oxime -TMS Derivative	Normal Molecular Weight	Deuterated Molecular Weight
Glycoaldehyde	219	220
Glyceraldehyde	321	323
Erythrose	423	426
Threose	423	426
Arabinose	525	529
Lyxose	525	529
Ribose	525	529
Xylose	525	529

Observed Mass Spectral Data:

Glycoaldehyde

Peak	Retention Time(Sec)
1	670-688
2	689-701

Peak 1: *m/e* 73, 100%; *m/e* 103, 10.86%; *m/e* 105, 5.15%; *m/e* 117, 3.02%; m/e 130, 6.49%; *m/e* 131,12.53%; *m/e* 132, 9.46%; *m/e* 133, 11.19%; *m/e* 147, 62.67%; *m/e* 177, 2.35%; *m/e* 205, 1.62%; *m/e* 207, 1.57%; *m/e* 219, 4.53%; *m/e* 220, 1.96%; m/e 221, 1.85%; m/e 222. 0.78%.

Peak 2: *m/e* 73, 100%; *m/e* 103, 28.65%; *m/e* 105, 7.15%; *m/e* 116, 4.61%; *m/e* 117, 3.32%; *m/e* 119, 2.80%; *m/e* 130,11.45%; *m/e* 131, 18.39%; *m/e* 132, 8.76%; *m/e* 133, 10.41%; *m/e* 147, 72,44%; *m/e* 204, 3,37%; *m/e* 205, 4.04%; *m/e* 206, 1.09%; *m/e* 207, 0.78%; *m/e* 220, 0.67%; *m/e* 221, 1.24%; *m/e* 222, 0.73%.

Glyceraldehyde

Peak	Retention Time(Sec)
1	1092-1107
2	1142-1175

Peak 1: *m/e* 73, 100%; *m/e* 100, 34.69%; *m/e* 101, 55.30%; *m/e* 103, 55.74%; *m/e* 105, 17.26%; *m/e* 117, 3.90%; *m/e* 118, 1.46%; *m/e* 119, 1.46%; *m/e* 133, 6.01%; *m/e* 147, 19.75%; *m/e* 189, 1.89%; *m/e* 191, 4,38%; *m/e* 192, 4.38%; *m/e* 202, 1.03%; *m/e* 205, 0.60%; *m/e* 219, 0.49%; *m/e* 220, 0.81%; *m/e* 253, 0.32%; *m/e* 321, 0.60%; *m/e* 322, 1.41%; *m/e* 324, 0.65%; *m/e* 325, 0.70;%; *m/e* 326, 0.43%; *m/e* 327, 0.43%.

Peak 2: *m/e* 73, 100%; *m/e* 100, 17.85%; *m/e* 103, 43.74%; *m/e* 105, 20.84%; *m/e* 117, 3.21%; *m/e* 118, 2.20%; *m/e* 119, 1.73%; *m/e* 133, 3.53%; *m/e* 147, 16.16%; *m/e* 163, 0.72%; *m/e* 164, 1.48%; *m/e* 192, 2.09%; *m/e* 205, 0.58%; *m/e* 206, 0.83%; *m/e* 207, 0.50%; *m/e* 208, 1.12%; *m/e* 218, 0.69%; *m/e* 220, 1.26%; *m/e* 221, 3.43%; *m/e* 236, 0.40%; *m/e* 266, 0.32%; *m/e* 306, 0.54%; *m/e* 307, 0.50%;

m/e 308, 0.61%; *m/e* 309, 0.32%; *m/e* 310, 1.26%; *m/e* 321, 0.61%; *m/e* 322, 0.50%; *m/e* 323, 0.58%; *m/e* 324, 0.72%; *m/e* 325, 1.05%.

Erythrose

Peak	Retention Time(Sec)
1	1428-1444
2	1446-1456
3	1478-1480

Peak 1: *m/e* 73, 100%; *m/e* 103, 86.12%; *m/e* 105, 35.19%; *m/e* 116, 6.69%; *m/e* 117, 9.42%; *m/e* 118, 4.69%; *m/e* 119, 1.86%; *m/e* 120, 2.73%; *m/e* 133, 6.44%; *m/e* 147, 32.71%; *m/e* 172, 9.79%; *m/e* 189, 2.11%; *m/e* 192, 3.97%; *m/e* 202, 2.85%; *m/e* 205, 1.12%; *m/e* 221, 0.99%; *m/e* 231, 2.11%; *m/e* 233, 1.12%; *m/e* 254, 0.62%; *m/e* 261, 0.62%; *m/e* 265, 1.24%; *m/e* 320, 1.98%; *m/e* 321, 1.49%; *m/e* 322 1.12%; *m/e* 336, 0.74%; *m/e* 364, 0.74%; *m/e* 411, 0.74%; *m/e* 423, 1.61%; *m/e* 424, 1.49%; *m/e* 426, 0.99%.

Peak 2: *m/e* 73, 100%; *m/e* 103, 59.23%; *m/e* 105, 9.58%; *m/e* 116, 2.45%; *m/e* 117, 2.10%; *m/e* 118, 1.87%; *m/e* 119, 1.64%; *m/e* 120, 1.87%; *m/e* 133, 6.89%; *m/e* 147, 35.63%; *m/e* 189, 1.17%; *m/e* 191, 4.09%; *m/e* 192, 3.50%; *m/e* 204, 2.22%; *m/e* 206, 0.82%; *m/e* 208, 0.93%; *m/e* 216, 2.92%; *m/e* 320, 9.81%; *m/e* 321, 3.86%; *m/e* 322, 1.99%; *m/e* 323, 1.64%; *m/e* 424, 0.70%.

Peak 3: *m/e* 73, 86.55%; *m/e* 103, 41. 82%; *m/e* 105, 10.55%; *m/e* 117, 32.36%; *m/e* 118. 21.82%; *m/e* 119, 8.73%; *m/e* 120, 8.00%; *m/e* 133, 7.64%; *m/e* 147, 100%; *m/e* 205, 7.27%; *m/e* 206, 5.09%; *m/e* 208, 3.27%; *m/e* 219, 5.45%; *m/e* 220, 4.73%; *m/e* 221, 2.91%; *m/e* 321, 4.00%; *m/e* 428, 2.18%.

Threose

Peak	Retention Time(Sec)
1	1458-1469
2	1491-1498

Peak 1: *m/e* 73, 100%; *m/e* 103, 68.01%; *m/e* 105, 36.95%; *m/e* 117, 12.82%; *m/e* 118, 8.10%; *m/e* 133, 7.93%; *m/e* 147, 39.80%; *m/e* 191, 5.01%; *m/e* 205, 1.69%; *m/e* 206, 2.04%; *m/e* 207, 0.87, *m/e* 208, 1.63%; *m/e* 221, 1.34%; *m/e* 234, 1.05%; *m/e* 288, 1.69%; *m/e* 320, 4.78%; *m/e* 322, 2.68%; *m/e* 323, 3.03%; *m/e* 324, 1.22%; *m/e* 333, 1.92%; *m/e* 423, 1.63%; *m/e* 424, 1.22%; *m/e* 425, 0.82%; *m/e* 428, 0.58%.

Peak 2: *m/e* 86.73%; *m/e* 103, 17.99%; *m/e* 105, 16.22%; *m/e* 116, 3.69%; *m/e* 117, 9.88%; *m/e* 118, 9.88%; *m/e* 119, 6.93%; *m/e* 120, 27.88%; *m/e* 147, 100%; *m/e* 192, 3.24%; *m/e* 205, 1.77%; *m/e* 207, 1.62%; *m/e* 208, 10.18%; *m/e* 219, 1.77%; *m/e* 220, 2.80%; *m/e* 221, 4.28%; *m/e* 222, 2.06%; *m/e* 258, 6.19%; *m/e* 321, 1.77%; *m/e* 322, 2.80%; *m/e* 323, 1.77%; *m/e* 324, 1.33%; *m/e* 413, 1.03%.

Pentoses

Peak	Retention Time(Sec)
1	1722-1734
2	1735-1741
3	1742-1753

Peak 1: *m/e* 73, 100%; *m/e* 103, 73.53%; *m/e* 105, 14.55%; *m/e* 116, 10.09%; *m/e* 117, 34.34%; *m/e* 118, 18.48%; *m/e* 119, 9.44%; *m/e* 133, 3.15%; *m/e* 147, 54.18%; *m/e* 172, 5.24%; *m/e* 189, 5.37%; *m/e* 191, 23.33%; *m/e* 202, 2.62%; *m/e* 205, 2.88%; *m/e* 206, 2.36%; *m/e* 217,

1.05%; *m/e* 218, 0.79%; *m/e* 221, 1.18%; *m/e* 256, 4.33%; *m/e* 260, 15.47%; *m/e* 345, 5.37%; *m/e* 450, 3.28%; *m/e* 460, 1.18%; *m/e* 525, 7.47%; *m/e* 526, 15.60%; *m/e* 527, 19.40%; *m/e* 528, 9.57%; *m/e* 529, 2.88%; *m/e* 530, 4.46%; *m/e* 531, 1.44%

Peak 2: *m/e* 73, 71.91%; *m/e* 103, 44.82%; *m/e* 105, 22.41%; *m/e* 116, 3.34%; *m/e* 117, 13.38%; *m/e* 118, 16.05%; *m/e* 120, 18.39%; *m/e* 133, 7.69%; *m/e* 147, 100%; *m/e* 172, 5.02%; *m/e* 182, 2.01%; *m/e* 205, 3.34%; *m/e* 206, 4.01%; *m/e* 207, 3.34%; *m/e* 208, 7.69%; *m/e* 217, 1.67%; *m/e* 232, 2.34%; *m/e* 266, 2.68%; *m/e* 321, 5.35%; *m/e* 322, 13.71%; *m/e* 323, 4.68%; *m/e* 324, 5.69%; *m/e* 325, 5.35%; *m/e* 423, 4.35%; *m/e* 424, 2.01%; *m/e* 453, 3.01%.

Peak 3: *m/e* 73, 74.38%; *m/e* 103, 33.06%; *m/e* 105, 21.76%; *m/e* 116, 6.06%; *m/e* 117, 12.95%; *m/e* 118, 15.43%; *m/e* 119, 7.16%; *m/e* 120, 16.80%; *m/e* 133, 7.71%; *m/e* 147, 100%; *m/e* 172, 2.75%; *m/e* 191, 3.03%; *m/e* 205, 4.96%; *m/e* 206, 4.96%; *m/e* 207, 2.48%; *m/e* 208, 3.58%; *m/e* 231, 4.68%; *m/e* 257, 2.75%; *m/e* 321, 7.44%; *m/e* 322, 8.26%; *m/e* 323, 4.96%; *m/e* 324, 4.13%; *m/e* 325, 4.41%; *m/e* 423, 2.48%; *m/e* 450, 2.48%; *m/e* 461, 1.93%; *m/e* 512, 1.93%; *m/e* 525, 2.48%; *m/e* 527, 1.93%.

Yield data from the various reactions was provided in Tables 2 through 5 of the results and discussion section of the thesis. These tables are reproduced here for clarity.

Table 2 (Repeated)

Actual Reaction Yields in mmol Units.

Reactants	Run	Glycoaldehyde	Glyceraldehyde	Erythrose	Threose
C +	1	0.04181	0.02048	0.01005	0.01640
H_2O(20ml)	2	0.06092	0.00845	0.00199	0.00359
	3	0.08066	0.01087	0.00243	0.00189
C +	1	0.04481	0.00763	0.00508	0.00924
H_2O(5ml)	2	0.02809	0.00962	0.00456	0.00449
	3	0.06818	0.00732	0.0381	0.00484
C +	1	0.07917	0.02931	0.00724	0.01070
D_2O	2	0.07017	0.01739	0.01331	0.00615
	3	0.06373	0.01392	0.00331	0.00505
	4	0.04010	0.01546	0.00611	0.00304
	5	0.07323	0.01272	0.00296	0.00396
	6	0.05870	0.01783	0.00403	0.00489
	7	0.06051	0.01272	0.00327	0.00397
C + H_2CO	1	0.06882	0.01316	0.01016	0.00810
+H_2O	2	0.04966	0.00210	—	—
	3	0.00944	0.00207	0.00131	0.00749
C + H_2CO	1	0.02445	0.00328	0.00032	0.00103
+D_2O	2	0.02949	0.01882	0.01014	0.00672

Table 3 (Repeated)

Standardized Reaction Yields

Reactants	Glycoaldehyde	Glyceraldehyde	Erythrose	Threose
C + H_2O(20ml)	0.0611±0.0194	0.0133±0.0064	0.0085±0.0070	0.0079±0.0068
C + H_2O(5ml)	0.0470±0.0201	0.0082±0.0012	0.0045±0.0006	0.0062±0.0026
C + D_2O	0.0639±0.0128	0.0170±0.0058	0.0057±0.0037	0.0054±0.0025
C + H_2CO +H_2O	0.0426±0.0303	0.0058±0.0063	0.0057±0.0063	0.0078±0.0004
C + H_2CO +D_2O	0.0270±0.0036	0.0110±0.0110	0.0067±0.0049	0.0039±0.0040
C + H_2O/D_2O	0.0592±0.0161	0.0141±0.0061	0.0053±0.0033	0.0060±0.0039
C + H_2CO +H_2O/D_2O	0.0364±0.0231	0.0079±0.0077	0.0091±0.0042	0.0058±0.0032

Table 4 (Repeated)

Yields of Reaction Products Relative to Glycoaldehyde.

Reactants	Run	Glycoaldehyde	Glyceraldehyde	Erythrose	Threose
C +	1	1.0000	0.48981	0.24037	0.39231
H_2O(20ml)	2	1.0000	0.13868	0.03272	0.05899
	3	1.0000	0.13475	0.03009	0.02348
C +	1	1.0000	0.17034	0.11346	0.20618
H_2O(5ml)	2	1.0000	0.34240	0.16246	0.15974
	3	1.0000	0.10743	0.05594	0.07109
C +	1	1.0000	0.37022	0.09139	0.13511
D_2O	2	1.0000	0.24777	0.18971	0.08771
	3	1.0000	0.21838	0.05194	0.04773
	4	1.0000	0.38560	0.15228	0.09890
	5	1.0000	0.17369	0.04043	0.05415
	6	1.0000	0.30378	0.06870	0.08338
	7	1.0000	0.21016	0.05404	0.06551
C + H_2CO	1	1.0000	0.19130	0.14768	0.11777
+H_2O	2	1.0000	0.04223	—	—
	3	1.0000	0.21942	0.13871	0.79355
C + H_2CO	1	1.0000	0.13404	0.01304	0.04199
+D_2O	2	1.0000	0.63824	0.34385	0.22789

Table 5 (Repeated)

Standardized Relative Yields

Reactants	Glycoaldehyde	Glyceraldehyde	Erythrose	Threose
C + H_2O(20ml)	1.0000	0.2544±0.2039	0.1011±0.1206	0.1583±0.2035
C + H_2O(5ml)	1.0000	0.2067±0.1216	0.1106±0.0533	0.1457±0.0686
C + D_2O	1.0000	0.2728±0.0822	0.0926±0569	0.0818±0.0299
C + H_2CO +H_2O	1.0000	0.1510±0.0952	0.1432±0.0063	0.4557±0.4778
C + H_2CO +D_2O	1.0000	0.3861±0.3565	0.1784±0.2339	0.1349±0.1314
C + H_2O/D_2O	1.0000	0.2533±0.1163	0.0987±0.0677	0.1142±0.0973
C + H_2CO + H_2O/D_2O	1.0000	0.2450±0.2300	0.1608±0.1366	0.2953±0.3408

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